A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Technical Progress Report
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EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-9

CONSOL received and partially completed analyses of 81 feed and process stream samples from HTI liquefaction bench run CMSL-9 (227-87). Reported here are highlights of characterization results obtained to date from these samples; a full report will be given later. Run CMSL-9 was operated entirely with dispersed catalyst and Black Thunder Mine coal, with and without mixed plastics or high density polyethylene (HDPE) as coprocessing feedstocks. Samples from the run were provided to DOE/PETC.

Interstage and pressure-filter liquid (PFL) or vacuum still overhead (VSOH) oils, and to a lesser degree, separator overhead (SOH) oils from coal-only periods with dispersed catalyst operation in Run CMSL-9, showed proton distributions that reflect a lower degree of hydrogenation than corresponding samples from thermal/catalytic Run CC-15 and from catalytic/ catalytic Run CC-1, both made with Black Thunder coal and supported catalyst.

A large amount of toluene was found in the period 19 VSOH sample; its presence may be related to preparation and use of dry, toluene-washed pressure-filter cake (PFC) from earlier in the run, which was used as the source of recycled Mo catalyst during Condition 4 (periods 15-19).

Separator overhead oils (SOHs) from many coal-only and coal/plastic periods contain sediments; the sediments have not been characterized. Relative amounts of n-paraffins as determined by gas chromatography-mass spectrometry (GC-MS) in the SOHs and 850 °F⁻ distillates from continuous atmospheric still (CAS) bottoms appear to increase according to the following trend: periods 5 and 29 (coal) < period 34 (coal/mixed plastics) < period 38 (coal/HDPE) and period 41 (coal/mixed plastics). Differences between the characteristics of SOHs from periods 34 and 41 may have resulted from the higher wt % plastics feed in period 41 (50 wt % vs 33 wt %), the use of vacuum distillation in period 34 vs pressure filtration in period 41, and the lack of ashy recycle in period 41.

The light color and low ash content of resid tetrahydrofuran (THF) insolubles from coal/plastics periods 38 and 41 CAS bottoms samples seem to indicate high HDPE concentration. The corresponding PFL samples were found to contain about 20 to 25 wt % THF insolubles, presumed to be incompletely converted HDPE. There was some evidence of phase separation on cooling of the distillation bottoms from one coal/mixed plastics period CAS bottoms sample. The layers were less distinct than was observed with the PFL resids obtained from Run CMSL-8. In general, the CAS bottoms samples from coal/plastics periods showed proton distributions consistent with the paraffinic character of the CAS bottoms and with increased hydrogenation when coal and plastics were fed, compared to corresponding samples from coal-only periods.

INSPECTION TESTS ON NET PRODUCTS FROM HTI RUNS POC-1 AND POC-2

A suite of inspection tests was performed on the net distillate products of HTI Runs POC-1 and POC-2. The samples tested were aliquots of the two materials tested by Southwest Research Institute (SwRI) under the DOE Refining and End Use Study of Coal Liquids project. Both oils are nearly devoid of metals and atmospheric resid and have very low sulfur and nitrogen contents. The fractions of both oils have excellent oxidation stability and excellent copper corrosion test performance. The octane numbers are comparable to those from straight-run petroleum naphthas. Although both oils appear to be of high quality as refinery feedstocks, the POC-2 oil is of higher quality.

RESID REACTIVITY

The fifteen resid samples being used in the resid reactivity study were separated by solubility and chromatographic techniques to provide information on the quantity of different classes of compounds found in the resids. This information will be used in construction of the resid reactivity model being developed by the University of Delaware under this contract. The sample fractions were sent to the University of Delaware where molecular weights will be determined by vapor phase osmometry (VPO). These molecular weight data also will be used in construction of the resid reactivity model.

Cross polarization/magic angle spinning (CP/MAS) ^{13}C-NMR spectrometry was used to analyze the resid reactivity sample set. A set of twelve carbon structural parameters and average molecular structural descriptors were derived for each

resid from the NMR analysis. These data will be used by Delaware in construction of the kinetic model of the reactivity of coal-derived resids.

Analysis of products of short-time batch reactor (STBR) studies performed at the University of Delaware show the samples to contain high manganese contents. It appears likely that the presence of Mn in the samples arises from abrasion or leaching of the reactor walls.

Section 2
INTRODUCTION

This is the Technical Progress Report for the fifth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period July 1 through September 30, 1995.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project will build on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods will be obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, analytical instruments and techniques which are currently underutilized for the purpose of examining coal-derived samples will be evaluated. The data obtained from this study will be used to help guide current process development and to develop an improved data base on coal and coal liquids properties. A sample bank will be established and maintained for use in this project and will be available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) will be examined. From the literature and data experimentally obtained, a mathematical kinetic model of resid conversion will be constructed. It is anticipated that such a model will provide insights useful for improving process performance and thus the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS QUARTER

- We completed many of the analyses on the 81 samples received from HTI bench-scale run CMSL-9, in which coal, coal/mixed plastics, and coal/high density polyethylene were fed. Analysis priority was given to the coal/plastics period samples, especially to the continuous atmospheric still (CAS) bottoms and separator overheads (SOH) streams. Highlights of results obtained to date appear in this report. Samples were distributed to DOE/PETC.

- A suite of inspection tests was completed on the net distillate products of HTI Runs POC-1 and POC-2. Results are described in the Discussion section of this report, and presented in Appendices 3 and 4.

- Liquid chromatographic separations of the 15 samples in the University of Delaware sample set were completed. The data were transmitted to Delaware for use in construction of the resid reactivity model. The experimental method used and results obtained are described in the Discussion section of this report.

- WRI completed CP/MAS ^{13}C-NMR analyses on the Delaware sample set. These data also will be used by Delaware in the kinetic model. The data are presented in Appendix 5 of this report.

- A review was made of elemental analyses obtained on 29 STBR product samples. Some of the samples have substantial amounts of manganese in the ash. The data are presented in the Discussion section of this report.

- A conference call was held with Delaware to discuss catalyst choice for future work.

- A visit was made to the University of West Virginia to discuss possible teaming arrangements.

- The University of Delaware continues to make good progress on the resid reactivity task; the Delaware Quarterly Report is appended to this report (Appendix 6).

ACTIVITIES IN PROGRESS

- Twenty-three samples were received from HTI bench-scale Run CMSL-10. Samples will be distributed to other research groups on request.

- Sets of samples were requested from HTI Run CMSL-11 (Appendix 1) and HTI Run POCB-1 (Appendix 2).

- In-house experimental work began on Task 1.4 Structure and Reactivity. The in-house work will supplement resid reactivity data being generated by the University of Delaware.

- Several different methods are being evaluated for separating or quantifying unconverted polyethylene in coal/waste co-liquefaction products and intermediate streams. The methods include hot filtration, petrographic and fluorescence microscopy, and flow field flow fractionation. Earlier work showed some utility in field ionization mass spectrometry and infrared spectroscopy.

Section 3
RESULTS AND DISCUSSION

PROGRESS OF CONSOL CHARACTERIZATION OF SAMPLES FROM HTI RUN CMSL-9
INTRODUCTION

CONSOL partially completed analyses of 81 feed and process stream samples from HTI bench Run CMSL-9. Reported below are highlights of characterization results obtained to date from these samples. Complete characterization results and analytical data will be reported at a later time. HTI liquefaction bench unit Run CMSL-9 (227-87) was operated with all-dispersed catalyst and Black Thunder Mine (Wyodak and Anderson seam) coal, with and without mixed plastics or high density polyethylene (HDPE) as coprocessing feedstocks. The dispersed catalysts used were Molyvan A and HTI's iron catalyst, a sulfated iron hydroxide.

SAMPLE DISTRIBUTION

A list of samples received from HTI Run CMSL-9 (81 samples from nine periods of operation) was provided to PETC and CFFLS. Thirty-three requested samples from one coal period and the three coal/plastics periods of Run CMSL-9 were provided to K. Rothenberger at DOE/PETC.

ANALYSIS STRATEGY

An overall analytical plan for samples from Run CMSL-9 was presented in the previous quarterly technical report.[1] HTI switched from solids separation by filtration to vacuum distillation early in the run, and then returned to filtration late in the run. There are difficulties in directly comparing vacuum still overheads (VSOHs) with pressure-filter liquids (PFLs), or vacuum still bottoms (VSBs) with pressure-filter cakes (PFCs), especially from coal/plastics liquefaction. This is because the unconverted HDPE is expected to be found in the PFL, but not in the VSOH (it melts and dissolves in the filtrate, but is non-distillable). For this reason, much of the early analytical effort was concentrated on the continuous atmospheric still (CAS) bottoms. The CAS bottoms is the feed stream to both filtration and vacuum distillation, and thus, is a good sample for comparison.

DISPERSED CATALYST OPERATION

Although a complete set of Run CMSL-9 sample analyses was not available, some results from coal-only dispersed catalyst operation in Run CMSL-9 were compared with data from other Black Thunder coal runs in which supported catalyst was used. Run CC-15 was operated in the thermal/catalytic configuration with Shell S-317 Ni/Mo supported extrudate catalyst in the second-stage reactor. The period of Run CC-15 used for this comparison (period 8) was made with a dispersed hydrous iron hydroxide catalyst precursor impregnated in the coal. Results are compared with those of previous HRI CTSL bench unit Run CC-1, which was operated in the catalytic/catalytic configuration, also with Shell S-317 catalyst. Period 16 of Run CC-1 was used for this comparison. The periods of Run CMSL-9 which were compared were periods 5 and 29, in which coal alone was the feedstock. Space velocity was approximately 50% higher in Run CMSL-9 than in Runs CC-1 and CC-15. Differences in other conditions would also affect oil characteristics.

Interstage and PFL or VSOH oils from all-dispersed catalyst operation in Run CMSL-9 were significantly more aromatic (25 to 30% vs. 15 to 20% aromatic protons), less hydroaromatic (12% vs ca. 17% cyclic beta protons), and less paraffinic (30 to 35% vs. 40 to 45% alkyl beta plus gamma protons) than corresponding oils from comparison periods of Runs CC-15 and CC-1. Furthermore, the SOH oils from all-dispersed catalyst operation in Run CMSL-9 which were exposed to supported catalyst in the in-line hydrotreater were more aromatic (9 to 16% vs ca. 6% aromatic protons), and less hydroaromatic (16 to 21% vs 22 to 24% cyclic beta protons) than corresponding oils from comparison periods of Runs CC-15 and CC-1. These differences reflect a lower degree of hydrogenation in the samples produced in the absence of supported catalyst in the liquefaction system. Factors other than dispersed catalyst use may have contributed to lower hydrogenation. Although these results indicate lower hydrogenation, HTI found SOHs from these periods of Runs CC-1 and CC-15 to be similar in H/C ratio and API gravity to the SOH from period 5 of Run CMSL-9.[2] Additional comparisons of properties of liquids produced with all-dispersed catalyst will be made when the analyses are complete.

TOLUENE FOUND IN PERIOD 19 VSOH

The presence of a large amount of toluene in the period 19 VSOH sample from HTI Run CMSL-9 was detected by proton NMR spectroscopy and gas chromatography-mass

spectrometry (GC-MS). V. Pradhan of HTI was informed about the presence of toluene in this sample. He indicated that the origin may have been distillation of a toluene-washed filter cake. This seems to have resulted somehow from preparation and use of dry, toluene-washed pressure-filter cake (PFC) from earlier in the run as the source of recycled Mo catalyst during Condition 4 (periods 15-19).

CHARACTERISTICS OF SOHs AND CAS BOTTOMS DISTILLATES

Separator overhead oils (SOHs) from many coal-only and coal/plastic periods contain sediments; the sediments have not been characterized. Sediment in the distillate product was previously observed only in the coal/plastics period of Run POC-2; it had not been previously observed, nor was it found in SOHs from Run CMSL-8.

SOHs and CONSOL-generated 850 °F⁻ distillates from continuous atmospheric still bottoms (CAS bottoms) samples from two coal-only periods and the three coal/ plastics periods were characterized by gas chromatography-mass spectrometry (GC-MS). Relative amounts of n-paraffins in the oils appear to increase according to the following trend: periods 5 and 29 (coal) < period 34 (coal/mixed plastics) < period 38 (coal/HDPE) and period 41 (coal/mixed plastics). CAS bottoms 850 °F⁻ distillates from periods 38 and 41 contain such high concentrations of paraffins that other components appear as only minor peaks in the GC-MS chromatogram. Paraffinic protons (alkyl beta and gamma) account for over 60% of the hydrogen in the period 41 CAS bottoms distillate.

CHARACTERISTICS OF CAS BOTTOMS AND PFLs

The period 38 CAS bottoms 850 °F⁺ distillation resid appeared to consist of two layers, but the layers were similar in appearance and not distinctly separable based on physical characteristics such as brittleness (i.e., they could not be easily separated by breaking). These materials are different from the distillation bottoms of CMSL-8 PFLS. In those samples, layers with distinctly different properties were observed to separate, as reported last quarter.[1]

The tetrahydrofuran (THF) insoluble portions of CAS bottoms 850 °F⁺ resid samples from periods 38 and 41 of the three Run CMSL-9 coal/plastics periods were light in color and low in ash content, most likely the result of a high HDPE concentra-

tion. In contrast, the corresponding period 34 sample was mostly black in color, but was inhomogeneous in appearance, with tan-colored particles in addition to black ones.

In general, the CAS bottoms samples from coal/plastics periods were lower in aromatic protons, lower in cyclic beta (hydroaromatic) protons, and higher in alkyl beta plus gamma protons (as a rough measure of paraffinic protons) than corresponding samples from coal-only periods. This seems to be consistent with the paraffinic character of the CAS bottoms and with the idea that the oils were more highly hydrogenated when coal and plastics were fed.

The PFL samples from coal/mixed-plastics periods 38 and 41 of HTI Run CMSL-9 were found to contain about 20 to 25 wt % THF insolubles, presumed to be incompletely converted HDPE.

INSPECTION TESTS ON NET PRODUCTS FROM HTI RUNS POC-1 AND POC-2

INTRODUCTION

A suite of inspection tests was performed on the net distillate products of HTI Runs POC-1 and POC-2. The testing plan (reported previously[3]) was formulated in conjunction with Dr. P.-Z. Zhou of Burns and Roe Services Co. The samples tested were aliquots of the two materials tested by Southwest Research Institute (SwRI) under the DOE Refining and End Use Study of Coal Liquids project (DOE Contract No. DE-AC22-93PC91029). The testing plan arranged by CONSOL included numerous tests, some which also are being conducted by SwRI on different aliquots of the same samples, and some which are not. Thus, the CONSOL test plan supplements the SwRI test plan as well as provides an independent check on it. The data provided here will be used to better define the value and the refining requirements of coal liquids.

SAMPLES AND TESTING

Two samples were provided to CONSOL by Mr. Jimell Erwin of SwRI:

1)   Net distillate product of HTI Run POC-1. Six gallons were provided in a 5 gal and a 1 gal metal can. They were received at CONSOL on 6/10/94 and bore an SwRI sample number FL-2236 (DL-1). HTI Run POC-1 (also known as Run 260-04) was conducted in late 1993 and early 1994 with Illinois 6 coal. Two ebullated-bed catalytic reactors were used. The in-line hydrotreater was in place, but slip-streaming prevented it from being effective.

2)   Net distillate product of HTI Run POC-2. Six gallons were provided in a 5 gal and a 1 gal metal can. The samples were shipped from SwRI on 10/13/94; the SwRI sample number was FL-2364 (DL-2). The assigned CONSOL sample number was 185-1621-33. HTI Run POC-2 (also known as Run 260-05) was conducted in June and July 1994 with Black Thunder Mine subbituminous coal. Two ebullated-bed catalytic reactors were used. The in-line hydro-treater was in place and operational.

The two samples were shipped for testing to Conoco Inc., Research and Engineering Dept., Ponca City, OK on March 14 and 16, 1995. The testing at Conoco was conducted under the direction of Mr. Dale Cabbiness. Conoco arranged to have the octane testing performed at Phillips Petroleum Co., Bartlesville, OK. Conoco's

complete reports appear as Appendices 3 and 4. The specific test methods used by Conoco appear at the end of each report. The D86 distillations were conducted with 100 mL samples. Thus, the volumes in mL (provided in the Conoco reports) are equivalent to volume %. Several explanatory notes are in order concerning the paraffins, olefins, naphthenes and aromatics (PONA) analyses conducted by Conoco. The olefins, aromatics, and paraffins plus naphthenes were determined by fluorescence indicator analysis (FIA) on the 180-350 °C, 350-400 °C, and 400-500 °C fractions. Paraffins, naphthenes, and aromatics also were determined by gas chromatography (GC) on a separate sample of all six fractions from the IBP-180 °C fraction to the 550-650 °C fraction. Any olefins present are accounted during the GC analysis as their saturated analog; i.e., either a paraffin or a naphthene. Thus, olefins may be doubly accounted if the olefin data from the FIA analysis are combined with the paraffin data from the GC analysis. However, more importantly, the GC method is unable to detect high-boiling components. Thus, the data from the GC method for the fractions with boiling points greater than 180 °C are incomplete.

DISCUSSION

Both materials are atmospheric distillates, 94 wt % or greater boils below 650 °F. The yields of the seven distillate fractions are quite similar for the two oils. Both yield about 28 wt % naphtha (IBP-350°F), about 9 wt % swing cut (350-400 °F), about 22 wt % kerosene (400-500 °F), about 37 wt % diesel fuel cut (500-650 °F), and about 5 wt % atmospheric resid (650 °F$^+$). Both oils are nearly devoid of metals and atmospheric resid and have very low sulfur and nitrogen contents. The fractions of both oils have excellent oxidation stability and excellent copper corrosion test performance. The octane numbers are comparable to those from straight-run petroleum naphthas. However, the fractions of both oils failed the JFTOT thermal stability test.

Although both oils appear to be of high quality as refinery feedstocks, the POC-2 oil is of higher quality. This is evidenced by the lower concentrations of nitrogen, basic nitrogen, sulfur, mercaptan sulfur, and oxygen, the lower aromatics and olefins contents, the lower existent gum results, and the higher hydrogen content and higher smoke point of the POC-2 whole oil or its fractions.

SARA (SATURATES, AROMATICS, RESINS, ASPHALTENES) SEPARATION

Separation of fifteen 850 °F+ coal-derived resid samples by solubility and chromatography separation techniques was carried out to provide information on the quantity of different classes of compounds found in the resids. This information will be used in construction of the resid reactivity model being developed by the University of Delaware under this contract. The sample fractions were sent to the University of Delaware, where molecular weights will be determined by vapor phase osmometry (VPO). These molecular weight data also will be used in construction of the resid reactivity model.

The separation technique used was requested by the University of Delaware to provide data for the modeling study in a form with which they are familiar. It is a variation on the SARA separation method.[4] In this scheme, the samples are separated into saturate, aromatic, resin, and asphaltene fractions which are defined as follows. Asphaltenes are defined as heptane insolubles; in the case of the resids separated in this work, this fraction also includes insoluble organic matter and mineral matter. The saturates, aromatics, and resins are fractionated on a silica gel liquid chromatography column. The saturates are eluted with heptane, the aromatics are eluted with a 50/50 vol % solution of heptane and toluene, and the resins are removed from the column with 50/25/25 vol % solution of methanol, toluene, and petroleum ether followed by neat petroleum ether.

The definition of the asphaltene fraction as a heptane-insoluble material is not consistent with the solubility definition commonly used by CONSOL. CONSOL's definition for the asphaltene fraction of coal liquids is the benzene-soluble, hexane-insoluble portion of the oil. Therefore, the asphaltene fraction isolated in the SARA method was further fractionated into toluene-soluble and toluene-insoluble fractions. The toluene insolubles then were fractionated into THF-solubles and THF-insoluble material (IOM and ash).

The detailed experimental procedure is provided in Section 4. Table 1 gives a description of the resids. Table 2 contains the separation data for the fifteen resid samples. There are no apparent correlations between the distribution of the fractions obtained in the separations and the known parameters associated with the samples such as feed coal, sampling location in the liquefaction plant,

or H/C ratio.   However, a clear distinction can be made between materials produced in the HTI facility and in the Wilsonville facility. The HTI materials (SARA Runs 14 and 15) contain about 4 to 10 times less asphaltene fraction and 2 to 20 times more saturates than the Wilsonville materials.

MANGANESE CONTAMINATION IN STBR PRODUCT SAMPLES

The solids portion of twenty-nine reaction products from experiments performed in Delaware's STBR were analyzed; the results of the analyses were provided previously[1] and are reproduced in Table 3. These samples were produced from the 850 °F+ resid of Wilsonville Run 258 V131 B (recycle stream) using either sulfided molybdenum naphthenate obtained from Shepherd Chemical Co. or sulfided Shell 324 Ni/Mo on alumina catalyst. A review of the ash elemental analyses showed the samples to contain an unexpectedly high Mn content (measured as MnO_2). The ash analysis of the starting resid was reviewed and the MnO_2 content was found to be <0.01 wt %. The two different catalysts used in Delaware's tests, the Shell 324 supported catalyst and the homogeneous molybdenum naphthenate catalyst were analyzed. The Shell 324 catalyst was found to contain <0.01 wt % MnO_2 in the ash. An analysis of the Mo naphthenate precursor was received from Shepherd Chemical Co.; the precursor contains <10 ppm Mn. Shepherd does not believe there was introduction of Mn in the production of the molybdenum form of the naphthenate. The CONSOL analysis of the Mo naphthenate catalyst confirms this; the MnO_2 content was found to be 0.03 wt % of the ash and the ash content of the sample was found to be 4.00 wt % of the sample. Renormalization of the sample data presented in Table 3 to a Ni/Mo-free basis was done for runs made with the Mo naphthenate. It also was done for data from runs made with the supported catalyst. In addition, the Al_2O_3 concentration was recalculated so that it would be equivalent to that found in the samples analyzed from the homogeneous catalyst tests (ca. 11 to 13 wt %). Recasting the data in this manner shows that the same amount (about 0.4 wt % of the ash) is MnO_2, regardless of the catalyst used. Because the Mn was not introduced with the resid or either of the two catalysts, it appears likely that the Mn arises from leaching or abrading of the reactor or associated tubing.

CROSS POLARIZATION/MAGIC ANGLE SPINNING (CP/MAS) ^{13}C-NMR ANALYSIS OF RESID SAMPLES

Fifteen direct coal liquefaction derived distillation resid materials (Table 1) were analyzed by Western Research Institute (WRI) using cross polarization/magic angle spinning (CP/MAS) ^{13}C-NMR spectrometry. From the NMR analysis, WRI derived a set of twelve carbon structural parameters for each resid (as per the method of Pugmire et al.[5]); these twelve parameters are listed in Table 4. Average molecular structural descriptors then were derived from these parameters; these eight descriptors are given in Table 5. These data will be used by the team at the University of Delaware who are constructing, under this contract, a kinetic model of the reactivity of coal-derived resids. WRI's findings are attached to this report as Appendix 5.

Section 4
EXPERIMENTAL

SARA SEPARATION

MATERIALS AND SUPPLIES

Quantities given are for one separation.

Equipment	Size	Materials and Supplies	Quantity
Soxhlet extractor		heptane, Fisher HPLC grade	3000 mL
heating mantle		toluene, Fisher HPLC grade	1250 mL
round-bottom flask	500 mL	methanol, Fisher HPLC grade	250 mL
rotary evaporator	500 mL	petroleum ether, Fisher Optima grade	750 mL
chromatography column with frit and		THF, freshly distilled	250 mL
reservoir	22 x 400 mm	silica gel, 70-230 mesh	150 mL
graduated cylinders	100 mL	Whatman filter paper, No. 42	80 mm
distillation flasks (4)	250 mL	washed sand	10 g
top loader balance		Soxhlet thimble, cellulose	26 X 60 mm
vacuum/drying oven			
watch glass			
Büchner funnel	85 mm		
filter flask	1000 mL		
vacuum tubing			
trap bottle			
aspirator			
Erlenmeyer flasks (2)	500 mL		
magnetic stirring bar			
magnetic stirrer			

ASPHALTENE FRACTION

Warm 200 mL of heptane to ~60 °C in a 500 mL Erlenmeyer flask. Mix 5 g of resid sample into the 200 mL of warm heptane. Mix for one hour keeping heptane at ~60 °C. Continue mixing with no heat for 18 h (overnight). Vacuum filter sample through weighed filter paper using Büchner funnel and Whatman 42 filter paper. Place filter paper and filter cake on tared watch glass in 50 °C oven to dry to constant weight. Scrape dried filter cake into tared Soxhlet thimble. Reweigh Soxhlet thimble and filter cake and calculate amount of material added to thimble. Extract filter cake in Soxhlet extractor with heptane until filtrate is clear. Depending on sample, this may take 48-72 hours. Combine heptane solubles from filter (filtrate) and Soxhlet extractor (extract). Rotovap the heptane-soluble solution in a tared flask, dry in 50 °C oven overnight, weigh and reserve the sample for column chromatography.* Dry the thimble and asphaltenes in a 50 °C oven, weigh, and reserve.

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*Note: After drying, this material is no longer completely heptane soluble.

SATURATE, AROMATIC, AND RESIN FRACTIONS

Activate 150 mL of silica gel in an oven at 150 °C for 18 h (overnight). Prepare 1000 mL total, 50 volume % heptane and 50 vol % toluene. Prepare 1000 mL total, 50 vol % methanol, 25 vol % toluene, and 25 vol % petroleum ether. Pack (20 mm x 400 mm) column which has a solvent reservoir with silica gel slurried in heptane. Mix heptane soluble material from filtration and Soxhlet extraction with about 10 mL of tetrahydrofuran (THF), add about 5-10 g clean washed sand. Rotovap off the THF, dry sample in vacuum oven at 50 °C for 12-18 hr to remove all THF. Scrape sample, now coated on sand, from flask. Apply dry granular sample to column. Wash sample remaining in flask from sand with THF, filter and dry. Calculate amount of sample applied to column.

Elute the saturates fraction with heptane. Collect 100 mL aliquots of eluent, rotovap each 100 mL in a tared 250 mL flask and record weight gain. When there is no detectable weight gain (<0.01 g), switch to 50:50 volume mixture of heptane and toluene to elute aromatics. Continue to collect 100 mL aliquots; rotovap aliquots in a second tared flask, and weigh. When weight gain is no longer detectable (<0.01 g), switch to 50:25:25 volume mixture of methanol, toluene, and petroleum ether to elute resins. Continue to collect 100 mL aliquots, rotovap in a third tared flask, and weigh. When no weight gain is detected (<0.01 g), switch to petroleum ether. Fill 250 mL column reservoir and collect petroleum ether fraction in an Erlenmeyer flask. Transfer to the same flask in which the methanol/toluene/petroleum ether fraction was collected. Dry and obtain weight. Dry contents of three flasks in oven at 50 °C under vacuum overnight, record final weights. Calculate percent of each fraction recovered.

ASPHALTENE SEPARATION INTO TOLUENE SOLUBLES, THF SOLUBLES, AND THF INSOLUBLES

Replace the Soxhlet thimble containing the heptane-insoluble fraction into the Soxhlet extractor with 200-225 mL toluene. Extract for 48-72 hours until extract is colorless. Remove thimble, dry in 50 °C vacuum oven 18 h (overnight). Weigh thimble with toluene insolubles. Remove toluene from soluble fraction on rotovap, dry in vacuum oven at 50 °C to constant weight. Return thimble to Soxhlet extractor with 200-225 mL THF. Extract in THF for 48-72 hours, until extract is colorless. Dry THF solubles on rotovap and then in vacuum oven at 50 °C for 18 hr; weigh. Dry thimble with THF insolubles in vacuum oven at 50 °C for 18 hr; weigh. Calculate percent toluene solubles, THF solubles, and THF insolubles.

CALCULATIONS

Asphaltenes (heptane insolubles):

$$\frac{\text{heptane insols (in Soxhlet thimble) (g)}}{\text{resid sample (g)}} \times 100 = \text{Asphaltenes (wt \%)}$$

Heptane solubles:

filtrate (g) + extract (g) = heptane solubles (g)

Column charge:

heptane sols (g) - residue in flask after removing sand (g) = column charge (g)

SARA fractions:

$$\frac{\text{Measured weight of recovered fraction (g)}}{\text{column charge (g)}} \times 100 = \text{\% of column charge}$$

% of column charge x heptane solubles (g) = fraction of heptane solubles (g)

$$\frac{\text{fraction of heptane solubles (g)}}{\text{resid sample (g)}} \times 100 = \text{fraction (wt \%)}$$

If Σ(fractions (g)) > column charge (g) and column packing is colorless, normalize to 100%.

If Σ(fractions (g)) < column charge (g), calculate loss on column.

Loss on column:

column charge (g) - (saturates (g) + aromatics (g) + resins (g)) = loss on column (g)

$$\frac{\text{loss on column (g)}}{\text{resid sample (g)}} \times 100 = \text{loss on column (wt \%)}$$

Overall loss/gain:

100% - (Saturates (wt %) + Aromatics (wt %) + Resins (wt %) +
Loss on Column (wt %) + Asphaltenes (wt %)) = Total Overall Loss/Gain (wt %)

Section 5
REFERENCES

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TABLE 1

SAMPLES FRACTIONATED BY SARA TECHNIQUE AND CHARACTERIZED BY ^{13}C-NMR

850°F$^+$ Distillation Resid Samples			
Run	Stream	SARA Run No.	Feed Coal (Seam/Mine)
Wilsonville 258	V 131B	1	Wyodak and Anderson/Black Thunder
Wilsonville 259	V 1067	11	Pittsburgh/Ireland
	R 1235	12	
	V 131B	13	
Wilsonville 260	V 1067	8	Wyodak and Anderson/ Black Thunder
	R 1235	9	
	V 131B	10	
Wilsonville 261	V 1067	3	Illinois No. 6/Burning Star No. 2
	R 1235	4	
	V 131B	2	
Wilsonville 262	V 1067	7	Wyodak and Anderson/ Black Thunder
	R 1235	5	
	V 131B	6	
HTI POC-1	O-43	14	Illinois No. 6/Burning Star No. 2
HTI POC-2	O-43	15	Wyodak and Anderson/Black Thunder

HTI = Hydrocarbon Technologies Inc.
W = Wilsonville
R 1235 = interstage steam
V 1067 = 2nd stage product stream
V 131B = recycle stream
O-43 = recycle stream

TABLE 2

SARA SEPARATION DATA

wt % Sample

RUN	1*	2	3	4	5	6	7	8	9	10*	11*	12	13	14	15
Saturates	1.5	5.1	2.6	7.6	4.5	6.1	6.9	2.9	6.1	4.4	6.1	1.8	2.1	16.4	25.2
Aromatics	23.4	38.0	20.7	29.4	15.4	20.8	21.9	20.4	26.3	28.4	22.7	26.5	31.2	53.1	50.3
Resins	10.6	7.4	20.7	4.2	16.8	11.7	9.1	19.9	7.9	8.0	11.0	11.2	14.5	23.0	11.3
Loss on column	-	4.0	-	1.7	1.9	2.9	4.1	-	-	-	-	3.5	4.9	0.4	0.9
Asphaltenes (Total)**	64.4	46.8	55.3	55.7	59.5	57.1	54.8	56.5	56.3	58.7	61.4	59.4	47.5	5.4	12.0
Asphaltenes (Toluene sols)	28.1	23.4	20.1	19.9	21.4	23.5	19.4	19.3	17.9	23.4	30.3	25.7	21.3	4.9	4.1
Asphaltenes (THF sols)	5.0	7.2	7.4	8.5	7.1	5.9	5.9	6.5	9.0	6.1	8.5	11.6	7.8	0.5	0.5
THF—Insols	31.3	16.2	27.8	27.3	31.1	27.7	29.5	30.7	29.4	29.3	22.7	22.0	18.4	ND	7.5
Total Overall Loss or Gain	-0.1	+1.3	-0.7	-1.4	-1.9	-1.4	-3.2	-0.3	-3.4	-0.5	+1.2	+2.4	+0.2	-1.7	-0.3

* (Normalized to 100% recovery from column)
** Including THF—Insols

Samples used in SARA separations

RUN #	Resid Sample Source
	(All samples are composite resids with the exception of HTI POC—1, which is from one run period)
1	W258, V—131B
2	W261, V—131B
3	W261, V—1067
4	W261, R—1235
5	W262, R—1235
6	W262, V—131B
7	W262, V—1067
8	W260, V—1067
9	W260, R—1235
10	W260, V—131B
11	W259, V—1067
12	W259, R—1235
13	W259, V—131B
14	HTI POC—01, O—43
15	HTI POC—02, O—43

HTI = Hydrocarbon Technologies Inc.
W = Wilsonville
R—1235 = interstage stream
V—1067 = 2nd stage product stream
V—131B = recycle stream
O—43 = recycle stream
ND = none detected

TABLE 3

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

Delaware Sample No.	COO1 (S)	COO2(S)	COO4(S)	COO6(S)	COO7(S)	COO8(S)	COO9(S)	CO14(S)	CO15(S)	CO17(S)
Ultimate, wt%										
C	58.71	59.32	53.27	51.22	53.08	55.55	46.94	52.82	49.43	53.15
H	2.76	2.60	2.33	2.24	2.24	2.43	2.16	2.46	2.29	2.59
N	1.08	1.11	1.01	0.99	1.04	0.91	0.85	0.84	0.86	0.94
S	3.21	3.20	3.57	3.92	3.82	4.49	5.77	3.79	3.82	3.58
Ash	39.27	34.48	42.71	44.97	43.50	40.13	49.50	43.78	46.68	42.20
O (by difference)	-5.03	-0.71	-2.89	-3.34	-3.68	-3.51	-5.34	-3.69	-3.23	-2.46
Ash Elementals, wt% of ash										
MoO_3	0.09	0.05	0.02	0.01	0.02	7.11	7.39	3.27	7.38	4.51
NiO	0.06	0.00	0.03	0.02	0.04	0.03	0.03	0.03	0.01	0.01
SiO_2	24.70	26.63	24.17	24.24	24.29	21.93	21.55	24.48	21.88	23.00
Al_2O_3	13.18	13.45	13.07	12.82	12.66	11.65	11.48	13.09	11.82	12.31
TiO_2	0.95	0.97	0.95	0.93	0.92	0.84	0.85	0.95	0.87	0.91
Fe_2O_3	21.99	21.95	21.04	20.82	20.82	19.45	18.91	21.67	19.86	19.81
CaO	14.25	14.47	14.28	14.26	13.92	12.42	12.95	12.55	12.83	13.37
MgO	3.41	3.42	3.40	3.37	3.32	2.73	2.98	2.75	3.03	3.16
Na_2O	1.84	1.84	1.88	1.79	1.83	1.54	1.59	1.63	1.65	1.74
K_2O	0.48	0.48	0.42	0.42	0.41	0.38	0.38	0.43	0.41	0.41
P_2O_5	0.60	0.59	0.59	0.59	0.57	0.47	0.46	0.57	0.47	0.51
SO_3	16.40	15.00	19.34	19.62	19.99	18.16	19.88	17.90	16.47	18.25
MnO_2	0.39	0.35	0.43	0.45	0.43	0.37	0.45	0.39	0.42	0.38
Unaccounted	1.66	0.79	0.38	0.66	0.78	2.92	1.10	0.29	2.90	1.63

TABLE 3 (Continued)

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

CONSOL Sample No.	356	357	358	359	360	361	362	363	364	365
Delaware Sample No.	COO18(S)	COO19(S)	CO20(S)	CO21(S)	CO22(S)	CO24(S)	CO25(S)	CO26(S)	CO27(S)	CO28(S)
Ultimate, wt%										
C	49.73	51.64	49.43	51.96	47.53	42.68	20.22	15.67	18.82	16.46
H	2.30	2.41	2.18	2.18	1.94	1.81	1.15	1.01	1.05	0.89
N	0.85	0.84	0.81	0.89	0.80	0.67	0.57	0.55	0.48	0.48
S	5.44	5.19	5.44	5.13	5.42	6.19	6.28	6.21	5.89	6.08
Ash	45.93	44.47	47.24	45.12	49.94	54.34	69.82	74.77	73.37	76.31
O (by difference)	-4.35	-4.55	-5.22	-5.28	-5.75	-5.84	1.67	1.55	0.14	-0.38
Ash Elementals, wt% of ash										
MoO_3	6.77	6.96	7.07	6.54	6.51	7.00	14.79	16.03	15.51	15.74
NiO	0.01	0.01	0.06	0.10	0.05	0.04	2.80	2.89	2.81	2.80
SiO_2	21.98	21.74	21.51	20.95	21.02	21.56	2.64	1.63	2.29	2.22
Al_2O_3	11.86	11.61	11.36	11.26	11.60	11.86	60.90	63.73	61.58	62.40
TiO_2	0.86	0.87	0.85	0.83	0.84	0.86	0.17	0.14	0.17	0.15
Fe_2O_3	19.73	19.13	20.09	21.08	19.05	19.32	2.83	1.62	2.21	2.04
CaO	12.22	12.32	12.52	12.90	12.41	12.82	1.62	1.07	1.46	1.35
MgO	2.84	2.97	2.96	2.89	3.07	3.14	0.37	0.24	0.34	0.30
Na_2O	1.67	1.68	1.64	1.61	1.63	1.67	0.25	0.16	0.24	0.21
K_2O	0.39	0.39	0.38	0.40	0.40	0.40	0.06	0.05	0.05	0.04
P_2O_5	0.46	0.46	0.44	0.43	0.48	0.48	6.94	7.26	7.05	7.15
SO_3	19.46	18.83	19.86	19.92	19.70	17.89	1.65	1.11	1.63	1.57
MnO_2	0.41	0.40	0.42	0.40	0.44	0.49	0.08	0.05	0.05	0.07
Unaccounted	1.34	2.63	0.84	0.69	2.80	2.47	4.88	4.02	4.59	3.96

TABLE 3 (Continued)

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

CONSOL Sample No.	366	367	368	369	370	371	372	373	374
Delaware Sample No.	CO29(S)	CO30(S)	CO31(S)	CO32(S)	CO33(S)	CO34(S)	CO35(S)	CO36(S)	CO37(S)
Ultimate, wt%									
C	22.21	15.87	17.80	18.71	18.03	17.47	57.23	42.88	24.03
H	1.00	0.82	0.94	0.83	0.81	0.76	2.31	1.50	1.14
N	0.51	0.42	0.44	0.45	0.41	0.44	1.06	0.71	0.58
S	5.51	6.29	6.07	5.98	5.84	5.76	3.20	4.34	5.86
Ash	71.56	76.73	74.78	74.99	75.62	76.00	38.71	55.94	67.71
O (by difference)	-1.00	-0.25	-0.15	-1.17	-0.90	-0.67	-2.51	-5.50	0.51
Ash Elementals, wt% of ash									
MoO_3	13.54	14.73	14.46	13.49	13.50	13.51	0.01	0.01	13.53
NiO	2.35	2.83	2.75	2.51	2.55	2.55	0.01	0.01	2.61
SiO_2	5.00	1.99	2.21	4.28	4.50	4.10	23.43	23.19	3.54
Al_2O_3	56.15	62.24	61.30	56.74	57.53	57.82	12.77	12.48	58.70
TiO_2	0.25	0.14	0.17	0.23	0.23	0.25	0.94	0.92	0.21
Fe_2O_3	4.59	1.80	2.37	4.18	4.11	4.03	20.93	20.66	3.44
CaO	2.93	1.22	1.58	2.75	2.65	2.61	14.02	13.80	2.29
MgO	0.67	0.26	0.35	0.61	0.63	0.61	3.38	3.26	0.53
Na_2O	0.39	0.17	0.23	0.35	0.37	0.35	1.85	1.79	0.32
K_2O	0.10	0.04	0.05	0.08	0.08	0.08	0.42	0.45	0.08
P_2O_5	6.73	7.26	7.02	6.36	6.37	6.43	0.59	0.59	6.62
SO_3	4.20	1.31	1.88	3.56	3.33	3.44	20.17	19.84	2.79
MnO_2	0.15	0.06	0.08	0.14	0.14	0.14	0.38	0.55	0.11
Unaccounted	2.96	5.95	5.55	4.73	4.02	4.09	1.10	2.45	5.24

TABLE 4

CARBON STRUCTURAL PARAMETERS
DETERMINED BY ^{13}C-NMR

Symbol	Fractions of sp^2-hybridized Carbon	Symbol	Fractions of sp^3-hybridized Carbon
f_a	total carbon	f_{al}	total carbon
$f_{a'}$	in an aromatic ring	f_{al}^H	CH or CH$_2$
f_a^C	carbonyl	f_{al}^*	CH$_3$ or nonprotonated
f_a^H	protonated and aromatic	f_{al}^O	bonded to oxygen
f_a^N	nonprotonated and aromatic		
f_a^P	phenolic or phenolic ether		
f_a^S	alkylated aromatic		
f_a^B	aromatic bridgehead		

TABLE 5

AVERAGE MOLECULAR STRUCTURAL DESCRIPTORS (LATTICE PARAMETERS)
DETERMINED BY ^{13}C-NMR

Symbol	Description	Symbol	Description
χ_b	mole fraction of condensed carbons;	B.L.	bridges and loops per cluster;
C	average aromatic cluster size	S.C.	side chains per cluster;
$\sigma+1$	number of attachments per cluster	MW	total molecular weight;
P_O	fraction of intact bridges;	M_δ	average molecular weight per

APPENDIX 1

SAMPLE REQUEST FOR HTI RUN CMSL-11

August 4, 1995

Dr. V. Pradhan
Hydrocarbon Technologies, Inc.
P. O. Box 6047
New York and Puritan Avenues
Lawrenceville, NJ 08648

Dear Vivek:

Our sample request for Run CMSL-11 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each CMSL-11 run condition: (1) 250 g of separator overhead (SOH) and 250 g of atmospheric still overhead (ASOH) or 250 g of SOH/ASOH blended in the correct product ratio; (2) 350 g of pressure-filter liquid (PFL); (3) 350 g of pressure-filter cake (PFC); (4) 350 g of continuous atmospheric still (CAS) bottoms; (5) 350 g of interstage sample (first-stage product); and (6) 250 g of feed slurry. Please also include: (7) 350 g of the start-up/make-up oil; (8) 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater; (9) a fresh 300 g sample of the feed coal; and (10) a 300 g sample of each plastic feedstock.

We have not yet received Run CMSL-10 samples, or the three interstage samples we were expecting from Run CMSL-8. We would appreciate any of these samples that you can provide.

Let us know of any problem areas with this request. Thank you for your assistance.

Sincerely,

G. A. Robbins
Sr. Research Chemist

cc: A. G. Comolli - HTI
      M. A. Nowak - PETC
      E. B. Klunder - PETC
      F. P. Burke
      R. A. Winschel
      S. D. Brandes

APPENDIX 2

SAMPLE REQUEST FOR HTI RUN POCB-1

September 18, 1995

Dr. V. Pradhan
Hydrocarbon Technologies, Inc.
P.O. Box 6047
New York and Puritan Avenues
Lawrenceville, NJ 08648

Dear Vivek:

Our sample request for POC Bench Option Run 1 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each run condition: (1) 250 g of separator overhead (SOH) and 250 g of atmospheric still overhead (ASOH) or 250 g of SOH/ASOH blended in the correct product ratio; (2) 350 g of pressure-filter liquid (PFL); (3) 350 g of pressure-filter cake (PFC); (4) 350 g of continuous atmospheric still (CAS) bottoms; (5) 350 g of interstage sample (first-stage product); and (6) 250 g of feed slurry. Please also include: (7) 350 g of the start-up/make-up oil; (8) 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater; (9) a fresh 300 g sample of each of the coal and petroleum resid feeds; and (10) 1 kg of the plastic feed.

Let us know of any problem areas with this request. Thank you for your assistance.

Sincerely,

G. A. Robbins
Sr. Research Chemist

GAR:ls

cc: A. G. Comolli - HTI
    M. A. Nowak - PETC
    E. B. Klunder - PETC
    F. P. Burke
    R. A. Winschel
    S. D. Brandes

APPENDIX 3

INSPECTION OF NET PRODUCTS OF HTI RUN POC-1

Technical Service Report

Project No.   ANA-119-95

To   R. A. Winschel, Consol Inc.

From   Dale Cabbiness

Date   September 18, 1995

Subject   **Light Oil Assay of C95028, Syn Products of CONSOL.**

This sample was received March 31, 1995 for special light oil analysis. The samples were precessed outside of the CONOCO standard Assay Management Process because of the special cut points and testing on the fractions. All data were run using ASTM, UOP or other standard methodology. Summary data and clarification information are attached.

Dale Cabbiness

TSR119.95

CC: Library and Arron Dillard

Conoco Sample Number: C95028   Consol Sample Number: FL2236 - POC-1

Test Required	Whole Oil or Cursory	1 IBP-180	2 180-350	3 350-400	4 400-500	5 500-550	6 550-650	7 650+	8 B 1-2 Blend	Cold Trap	Still Wash	Total Yield
API Gravity	32.2	63.8	47.2	34.2	28.2	23.9	21.8	18.7	49.6			
Specific Gravity	0.8643	0.7245	0.7919	0.8542	0.8860	0.9103	0.9228	0.9420	0.7812			
Aniline Point, °F					83	92	103	130				
Concarb, Wt%								0.4				
Metals: ppm												
Vanadium	<1											
Nickel	<0.5											
Iron	3.7											
Copper	<0.5											
Zinc	<1											
Ash, Wt%	0.00											
RVP, psig		7.06	1.15	0.12	0.12							
Smoke Point, mm				13.7	11.8							
Flash Point, °F				134	180	250						
Pour Point, °F				<-55	<-60	-45	-5	35				
Freeze Point, °F	-60			<-60	-55							
Basic Nitrogen, Wt %					0.051	0.037	0.033	0.058				
Mercaptan Sulfur, Wt%				0.007	0.004							
Luminometer #				27.2	22.0							
Paraffins, Vol% (GC)		31.68	16.98	6.57	0.94	0.39	0					
Naphthenes, Vol% (GC)		65.74	65.21	18.22	0.36	0.13	0					
Aromatics, Vol% (GC)		2.58	11.71	31.19	1.37	0	0					
Olefins, Vol% (FIA)			5	3.8	4							
Benzene, Vol%		2.58										
Naphthalenes, Vol%				1	2.6							
Pona		Data attached:										
Thermal Stability				FAIL / 4	FAIL / 4							
Research Octane #		77.90	62.57	65.24								
Motor Octane #		74.42	60.15	62.83								
Cetane Index				20.57	26.90	31.90	34.67					
Net Heat of Combustion				18120	18020				18250			
Acidity, mg KOH/g	0.12			0.01	<.01				0.02			
Copper Corrosion				1A	1A	1A			1A			
Existent Gum				16.8	9.4	7.6			14.8			
Oxidation Stability				OK-16hrs	OK-16hrs	OK-16hrs			OK-16hrs			
Total Carbon, Wt%	86.9		85.7	86.7	87.3	87.7	87.8	87.7				
Total Hydrogen, Wt%	12.59		13.66	12.64	12.13	11.9	11.86	11.6				
Total Nitrogen, Wt%	0.058	0.006	0.023	0.059	0.066	0.055	0.053	0.13				
Total Oxygen, Wt%	0.2		0.3	0.4	0.2	0.1	0.1	0.2				
Total Sulfur, Wt%	0.049	0.011	0.049	0.036	0.03	0.022	0.018	0.061				
Kinematic Viscosity, -4 °F				4.35	10.71							
Kinematic Viscosity, 104 °F				1.065	1.914	3.71	7.178					
Kinematic Viscosity, 210 °F					0.81	1.3	1.975	3.686				
Yield												
Weight % Recovered		4.53	22.77	8.16	21.93	15.51	20.77	5.58		0.12	0.19	99.56
Volume % Recovered		5.40	24.85	8.26	21.39	14.73	19.45	5.12		0.18	0.18	99.55
D86 Distillation, temp °F	°F	°F	°F	°F	°F	°F	°F					
IBP	132.6	102.0	216.8	348.4	400.0	458.2	454.8					
5 ML	196.8	121.4	216.8	368.2	430.0	458.2	553.4					
10 ML	232.7	134.9	236.1	369.1	424.0	516.5	567.8					
20 ML	291.9	141.4	242.0	370.4	434.0	515.8	577.9					
30 ML	353.8	146.8	250.1	371.4	438.0	518.9	579.9					
40 ML	407.6	151.3	258.4	372.9	441.0	518.5	581.9					
50 ML	451.7	155.4	268.8	374.7	445.0	520.1	584.4					
60 ML	491.9	159.2	281.3	376.8	449.0	522.5	587.4					
70 ML	522.8	162.8	294.4	379.2	456.0	524.8	590.9					
80 ML	550.7	166.1	307.4	382.2	461.0	528.9	594.8					
90 ML	582.4	170.0	321.0	386.7	469.0	535.6	604.5					
95 ML	605.3	173.8	330.0	390.3	484.3	541.4	617.5					
FINAL VOL.	636.0	195.6	366.0	400.8	490.0	555.2	628.6					
RECOVERY, Vol%	99.3	96.2	94.9	98.5	98.2	98.1	98.2					

Sample 8 was produced by combining cuts 1 and 2 in their yield ratios.
Separation was performed using ASTM 2892, 18 plate column.
All test were run using ASTM, UOP or equivalent Conoco Methods.
Thermal Stability: failed tube rating of 4 (highest value)

FIA Test Data	Oil or	1	2	3	4	5	6	7	8 B	Trap	Wash	Yield
Olefins, Vol%			5	3.8	4							
Aromatics, Vol%			13	29.8	44							
Paraffin + Naphthenes, Vol%			82	66.4	52							

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\002F0201.D
Instrument    : 1                          Vial       :   2
Operator      : BECKY SHAVER               Injection  :   1
Acquired on   : 08 Aug 95   02:05 PM       Seq. line  :   2
Processed on  : 16 Aug 95    8:28 AM
Sample name   : C95028-1
Methodname    : MOD1011.MTH


================================================================
Calculation of RON = 76.00

*** Remark : RON value is out of specified range. ***
Valid range is 94 < Ron < 103
================================================================
      ==========================================================
                    REPORT IN WEIGHT %
      ==========================================================
      C-num  Naphtenes   Paraffins    Aromatics    Totals
           =====================================================
         3     0.00        0.00         0.00         0.00
         4     0.00        0.00         0.00         0.00
         5     4.68        0.00         0.00         4.68
         6    59.35       24.18         2.86        86.39
         7     3.84        4.95         0.00         8.79
         8     0.00        0.00         0.00         0.00
         9     0.13        0.00         0.00         0.13
        10     0.00        0.00         0.00         0.00
        11     0.00        0.00         0.00         0.00
           =====================================================
      Totals 68.01       29.13         2.86       100.00

                          -------
      Total                100.00



      ==========================================================
                    REPORT IN VOLUME %
      ==========================================================
      C-num  Naphtenes   Paraffins    Aromatics    Totals
           =====================================================
         3     0.00        0.00         0.00         0.00
         4     0.00        0.00         0.00         0.00
         5     4.63        0.00         0.00         4.63
         6    57.28       26.47         2.58        86.33
         7     3.70        5.21         0.00         8.92
         8     0.00        0.00         0.00         0.00
         9     0.13        0.00         0.00         0.13
        10     0.00        0.00         0.00         0.00
        11     0.00        0.00         0.00         0.00
           =====================================================
      Totals 65.74       31.68         2.58       100.00

                          -------
      Total                100.00
```

```
=============================================================
                           PIONA
=============================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\003F0301.D
Instrument    : 1                        Vial      :   3
Operator      : BECKY SHAVER             Injection :   1
Acquired on   : 08 Aug 95  03:20 PM      Seq. line :   3
Sample name   : 028-2
Methodname    : MOD1011.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0808A.SEQ

=============================================================
Calculation of RON = 81.10

*** Remark : RON value is out of specified range. ***
Valid range is 94 < Ron < 103
=============================================================
    =========================================================
                     REPORT IN WEIGHT %
        =====================================================
C-num  Naphtenes   Paraffins    Aromatics    Totals
        =====================================================
   3      0.00        0.00         0.00         0.00
   4      0.00        0.00         0.00         0.00
   5      0.00        0.00         0.00         0.00
   6      5.24        0.41         0.14         5.78
   7     19.45        3.93         2.46        25.84
   8     16.92        4.23         3.56        24.71
   9     15.24        3.50         6.19        24.94
  10      7.51        2.61         0.00        10.13
  11      0.56        1.14         0.00         1.70
        =====================================================
Totals 64.93        15.83        12.35        93.10

PolyNaphthene               6.90
                          -------
Total                     100.00


        =====================================================
                     REPORT IN VOLUME %
        =====================================================
C-num  Naphtenes   Paraffins    Aromatics    Totals
        =====================================================
   3      0.00        0.00         0.00         0.00
   4      0.00        0.00         0.00         0.00
   5      0.00        0.00         0.00         0.00
   6      5.36        0.47         0.13         5.96
   7     19.86        4.39         2.36        26.61
   8     17.06        4.58         3.38        25.02
   9     15.16        3.69         5.84        24.69
  10      7.24        2.70         0.00         9.94
  11      0.53        1.15         0.00         1.68
        =====================================================
```

```
Totals 65.21        16.98          11.71            93.90
PolyNaphthene                 6.10
                           -------
Total                        100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\004F0401.D
Instrument      : 1                    Vial        :    4
Operator        : BECKY SHAVER         Injection   :    1
Acquired on     : 08 Aug 95  04:34 PM  Seq. line   :    4
Sample name     : 028-3
Methodname      : MOD1011.MTH
Sequencename    : C:\HPCHEM\1\SEQUENCE\P0808A.SEQ

================================================================
Calculation of RON = 100.20

================================================================
    ============================================================
                     REPORT IN WEIGHT %
    ============================================================
    C-num  Naphtenes   Paraffins    Aromatics      Totals
        ========================================================
         3     0.00        0.00         0.00         0.00
         4     0.00        0.00         0.00         0.00
         5     0.00        0.00         0.00         0.00
         6     0.00        0.00         0.00         0.00
         7     0.13        0.00         0.00         0.13
         8     0.00        0.00         0.00         0.00
         9     0.51        0.00         9.31         9.83
        10     6.65        0.43        17.37        24.45
        11    10.47        5.62         4.20        20.29
        ========================================================
    Totals 17.76          6.05        30.89        54.69

    >200                        20.09
    PolyNaphthene               25.22
                              -------
    Total                      100.00


    ============================================================
                     REPORT IN VOLUME %
    ============================================================
    C-num  Naphtenes   Paraffins    Aromatics      Totals
        ========================================================
         3     0.00        0.00         0.00         0.00
         4     0.00        0.00         0.00         0.00
         5     0.00        0.00         0.00         0.00
         6     0.00        0.00         0.00         0.00
         7     0.14        0.00         0.00         0.14
         8     0.00        0.00         0.00         0.00
         9     0.55        0.00         9.43         9.98
        10     6.89        0.47        17.45        24.81
        11    10.65        6.10         4.32        21.06
        ========================================================
    Totals 18.22          6.57        31.19        55.99
```

>200	20.05
PolyNaphthene	23.96

Total	100.00

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\005F0501.D
Instrument    : 1                        Vial      :   5
Operator      : BECKY SHAVER             Injection :   1
Acquired on   : 08 Aug 95  05:49 PM      Seq. line :   5
Sample name   : 028-4
Methodname    : MOD1013.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0808A.SEQ

         ===================================================
                        REPORT IN WEIGHT %
         ===================================================
         C-num  Naphtenes   Paraffins   Aromatics    Totals
               ==========================================
            3     0.00        0.00        0.00        0.00
            4     0.00        0.00        0.00        0.00
            5     0.00        0.00        0.00        0.00
            6     0.00        0.00        0.00        0.00
            7     0.00        0.00        0.00        0.00
            8     0.24        0.00        0.00        0.24
            9     0.00        0.17        0.00        0.17
           10     0.09        0.00        1.36        1.45
           11     0.00        0.68        0.00        0.68
               ==========================================
         Totals   0.33        0.85        1.36        2.55

         >200                   96.12
         PolyNaphthene           1.34
                               -------
         Total                 100.00


         ===================================================
                        REPORT IN VOLUME %
         ===================================================
         C-num  Naphtenes   Paraffins   Aromatics    Totals
               ==========================================
            3     0.00        0.00        0.00        0.00
            4     0.00        0.00        0.00        0.00
            5     0.00        0.00        0.00        0.00
            6     0.00        0.00        0.00        0.00
            7     0.00        0.00        0.00        0.00
            8     0.26        0.00        0.00        0.26
            9     0.00        0.20        0.00        0.20
           10     0.10        0.00        1.37        1.47
           11     0.00        0.74        0.00        0.74
               ==========================================
         Totals   0.36        0.94        1.37        2.67

         >200                   96.05
         PolyNaphthene           1.28
                               -------
         Total                 100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\006F0601.D
Instrument    : 1                    Vial       :   6
Operator      : BECKY SHAVER         Injection  :   1
Acquired on   : 08 Aug 95  07:04 PM  Seq. line  :   6
Sample name   : 028-5
Methodname    : MOD1013.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0808A.SEQ

        ==========================================================
                      REPORT IN WEIGHT %
        ==========================================================
        C-num  Naphtenes   Paraffins   Aromatics    Totals
               ===========================================
          3      0.00        0.00        0.00         0.00
          4      0.00        0.00        0.00         0.00
          5      0.00        0.00        0.00         0.00
          6      0.00        0.00        0.00         0.00
          7      0.00        0.00        0.00         0.00
          8      0.00        0.00        0.00         0.00
          9      0.00        0.09        0.00         0.09
         10      0.13        0.00        0.00         0.13
         11      0.00        0.27        0.00         0.27
               ===========================================
        Totals   0.13        0.36        0.00         0.48

        >200                  99.52
                             -------
        Total                100.00


        ==========================================================
                      REPORT IN VOLUME %
        ==========================================================
        C-num  Naphtenes   Paraffins   Aromatics    Totals
               ===========================================
          3      0.00        0.00        0.00         0.00
          4      0.00        0.00        0.00         0.00
          5      0.00        0.00        0.00         0.00
          6      0.00        0.00        0.00         0.00
          7      0.00        0.00        0.00         0.00
          8      0.00        0.00        0.00         0.00
          9      0.00        0.11        0.00         0.11
         10      0.13        0.00        0.00         0.13
         11      0.00        0.29        0.00         0.29
               ===========================================
        Totals   0.13        0.39        0.00         0.53

        >200                  99.47
                             -------
        Total                100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0808A\007F0701.D
Instrument      : 1                      Vial        :  7
Operator        : BECKY SHAVER           Injection   :  1
Acquired on     : 08 Aug 95  08:19 PM    Seq. line   :  7
Sample name     : 028-6
Methodname      : MOD1013.MTH
Sequencename    : C:\HPCHEM\1\SEQUENCE\P0808A.SEQ

        ========================================================
                      REPORT IN WEIGHT %
        ========================================================
        C-num  Naphtenes   Paraffins   Aromatics    Totals
           ======================================================
            3     0.00        0.00        0.00        0.00
            4     0.00        0.00        0.00        0.00
            5     0.00        0.00        0.00        0.00
            6     0.00        0.00        0.00        0.00
            7     0.00        0.00        0.00        0.00
            8     0.00        0.00        0.00        0.00
            9     0.00        0.00        0.00        0.00
           10     0.00        0.00        0.00        0.00
           11     0.00        0.00        0.00        0.00
           ======================================================
        Totals   0.00        0.00        0.00        0.00

        >200                    100.00
                                -------
        Total                   100.00


        ==========================================================
                       REPORT IN VOLUME %
        ==========================================================
        C-num  Naphtenes   Paraffins   Aromatics    Totals
           ======================================================
            3     0.00        0.00        0.00        0.00
            4     0.00        0.00        0.00        0.00
            5     0.00        0.00        0.00        0.00
            6     0.00        0.00        0.00        0.00
            7     0.00        0.00        0.00        0.00
            8     0.00        0.00        0.00        0.00
            9     0.00        0.00        0.00        0.00
           10     0.00        0.00        0.00        0.00
           11     0.00        0.00        0.00        0.00
           ======================================================
        Totals   0.00        0.00        0.00        0.00

        >200                    100.00
                                -------
        Total                   100.00
```

DU PONT

Analysis Report   Date September 6, 1995

To   D. K. Cabbiness

From   A.W. Buchholz Jr., CCAS, PCL

Phone   DuCom 442-5708

Subject (Sample Description)   Heat of Combustion Data

Analysis Codes G-BTU, N-BTU	Sample Numbers	Analytical Numbers	Reference Numbers
Charge Number 7003-0000-T002	C95028-3 C95028-4 C95029-3 C95029-4 C95029-8 C95029-8A	7391	AWB A400-60
Method LECO oxygen bomb calorimetry			
Reviewed by: A.W. Buchholz Jr.			

The samples were combusted using a LECO AC-300 oxygen bomb calorimeter which was calibrated using benzoic acid. No combustion aids were needed for the analyses. The condensed combustion products were rinsed from the combustion vessel and titrated for acid formation. Only a small amount of acid was titrated which was probably formed from the nitrogen in the air trapped inside the bomb. A small correction was made for the formation of nitric acid. Corrections for the combustion of the fuse wire were also made.

Water originally in the sample and the water formed in the combusiton reaction are both assumed to vaporize and then condense during the analysis releasing the heat of water vaporization back to the system. The gross heats of combustion or high heating values reported here include the heat released during condensation of the water vapor. The net heat of combustion or low heating values account for the loss of the water heat of vaporization. The net values more closely approximate the heat available to a boiler when a fuel is burned where the water vapor escapes through a flue and the heat of vaporization is not recovered.

Thanks.

A.W. Buchholz Jr.
Sr. Research Chemist

GROSS AND NET HEATS OF COMBUSTION VALUES

SAMPLE NO.	GROSS HEAT OF COMBUSTION G-BTU (BTU/LB)	AVERAGE G-BTU (BTU/LB)	NET HEAT OF COMBUSTION N-BTU (BTU/LB)	AVERAGE N-BTU (BTU/LB)
C95028-3	19,280 19,270	19,280	18,130 18,120	18,120
C95028-4	19,130 19,120	19,130	18,020 18,020	18,020
C95028-8	19,510 19,500	19,510	18,250 18,240	18,250
C95029-3	19,570 19,540	19,550	18,370 18,340	18,350
C95029-4	19,380 19,390	19,380	18,220 18,230	18,220
C95029-8B	19,700 19,670	19,690	18,410 18,380	18,400

Corporate Center for Analytical Sciences (CCAS), Ponca City Laboratories
P.O. Box 1267, Ponca City, OK 74602-1267

Phillips Technology Services
Facilities for Research, Development and Manufacturing

Fuel Octane Testing

January 27, 1995
Kok-6-95

Dale K. Cabbiness
Director, Analytical Services Section
Conoco, Inc.
1000 S. Pine
Ponca City, OK 74603

Dear Dale:

You had asked for a brochure or report concerning Phillips' capability for determining octane number by engine testing using small quantities of fuel. Attached is a description of our Knock Engine Automation System (KEAS) technology that makes it possible to use smaller quantities of fuel, and that also improves the quality of test data.

If you have additional technical questions you can direct them to Vance Kopp at (918) 661-9476. We are considering licensing the KEAS technology. If you would like to know more about this option, please contact Delmar Johnson at (918) 661-0620.

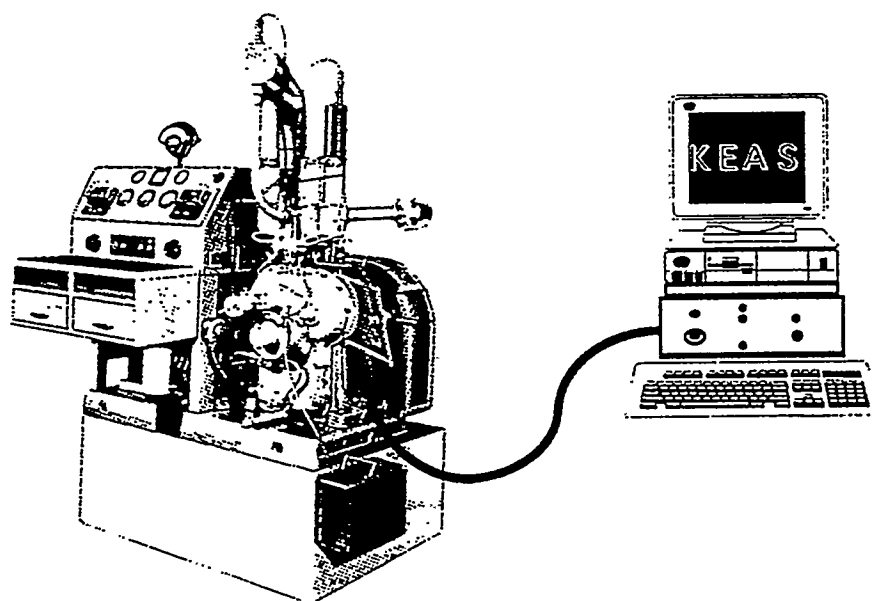Cordially yours,

Fritz C. Kokesh
Director, Technology Acquisition

Attachment

Phillips Corporate Technology
Phillips Petroleum Company
130 RF PRC
Bartlesville, OK 74004

918-661-3407
918-661-7353 (fax)

Knock Engine Automation System
KEAS

Ver 2.1

Knock Engine Automation System Summary

The KEAS system was developed in the 1980's. It was used initially to determine octane on small quantity samples. The KEAS system utilizes a 80486 IBM AT compatible computer with data acquisition hardware and software. The result is a PC-based control system for the knock engine. The software allows the operator to access the data acquisition capabilities of the computer through user-friendly graphical interfaces. On-line help is available throughout the program. Training of knock engine operators is dramatically simplified and reduced when utilizing this system. This allows refinery operations or other personnel to operate the engines, if necessary. In addition, the KEAS system is easily interfaced to laboratory information systems or local area networks, which facilitates the electronic transfer of data to refinery personnel or databases.

The KEAS system requires about 6 minutes to complete an octane test. It will run two octanes in 8 minutes and duplicates on two samples in 15 minutes. A single determination using standard ASTM procedure takes approximately 30 minutes. The repeatability of this test method should meet or exceed that of the standard ASTM method. The reproducibility of this method is currently under investigation.

The KEAS system is designed to allow the operator to select the mode of operation. It can be used in a fully automatic configuration or the KEAS system can be bypassed and the engine will operate in the standard mode as specified by the test method. The system also allows the operator to monitor critical engine parameters during the test and notifies the operator of an unusual condition.

If you would like further information or a demonstration of the system, please contact your Phillips representative.

Knock Engine Automation System
KEAS

- 50 ml Sample Volume
- Reduced sample turnaround
- Increased sampling frequency
- Interfaces with existing engines and LIMS

Test methods user for Assay:

Conoco Sample Number: C95028 **Consol Sample Number: FL2236 - POC-1**
Conoco Sample Number: C95029 **Consol Sample Number: FL2364 - POC-2**

Test Required	Method used:
API Gravity	ASTM D 4052
Specific Gravity	ASTM D 4052
Aniline Point, °F	ASTM D 611
Concarb, Wt%	ASTM D 4530
Metals: ppm	
Vanadium	Ash and ICP
Nickel	Ash and ICP
Iron	Ash and ICP
Copper	Ash and ICP
Zinc	Ash and ICP
Ash, Wt%	ASTM D 482
RVP	ASTM D 323
Smoke Point, °F	ASTM D 1322
Flash Point, °F	ASTM D 56 and D 93
Pour Point, °F	ASTM D 97
Freeze Point, °F	ASTM D 2386
Basic Nitrogen, Wt %	UOP 269 - 90
Mercaptan Sulfur, Wt%	UOP 163-59 / ASTM D 3227
Luminometer #	ASTM D 1740
Paraffins, Vol%	Analytical Controls Method
Naphthenes, Vol%	Analytical Controls Method
Aromatics, Vol%	Analytical Controls Method
Olefins, Vol%	ASTM D1319
Benzene, Vol%	Analytical Controls Method
Naphthalene, Wt%	ASTM D 1840
Pona	Analytical Controls Method
Thermal Stability	ASTM D 3241
Research Octane #	Phillips Technology Services, KEAS
Motor Octane #	Phillips Technology Services, KEAS
Cetane Index	ASTM D 976
Net Heat of Combustion	ASTM D 4529
Acidity, mg KOH/g	ASTM D 974
Copper Corrosion	ASTM D 130
Existent Gum	ASTM D 381
Oxidation Stability	ASTM D 525
Total Carbon, Wt%	Combustion using Leco CHNS - 932
Total Hydrogen, Wt%	Combustion using Leco CHNS - 932
Total Nitrogen, Wt%	ASTM D 4629
Total Oxygen, Wt%	Combustion using Leco RO - 478
Total Sulfur, Wt%	ASTM 4294
Kinematic Viscosity, -4 °F	ASTM D 445
Kinematic Viscosity, 104 °	ASTM D 445
Kinematic Viscosity, 210 °	ASTM D 445
Yield	ASTM D 2892
Weight % Recovered	ASTM D 2892
Volume % Recovered	ASTM D 2892
D86 Distillation, temp °F	ASTM D 86

APPENDIX 4

INSPECTION OF NET PRODUCTS OF HTI RUN POC-2

Technical Service Report

Project No.   ANA-120-95

To   R. A. Winschel, Consol Inc.

From   Dale Cabbiness

Date   September 18, 1995

Subject   **Light Oil Assay of C95029, Syn Products of CONSOL.**

This sample was received March 31, 1995 for special light oil analysis. The samples were precessed outside of the CONOCO standard Assay Management Process because of the special cut points and testing on the fractions. All data were run using ASTM, UOP or other standard methodology. Summary data and clarification information are attached.

Dale Cabbiness

TSR120.95

CC: Library and Arron Dillard

Conoco Sample Number: C95029   Consol Sample Number: FL2364 - POC-2

Test Required	Whole Oil or Cursory	1 IBP-180	2 180-350	3 350-400	4 400-500	5 500-550	6 550-650	7 650+	8 B 1-2 Blend	Cold Trap	Still Wash	Total Yield
API Gravity	33.7	62.0	49.3	36.3	29.9	25.0	22.1	20.4	51.3			
Specific Gravity	0.8567	0.7314	0.7826	0.8435	0.8765	0.9040	0.9214	0.9314	0.7742			
Aniline Point, °F					105	111	128	130				
Concarb, Wt%								0.04				
Metals: ppm												
Vanadium	<1											
Nickel	<0.5											
Iron	<0.5											
Copper	<0.5											
Zinc	<1											
Ash, Wt%	0.00											
RVP, psig		5.77	1.06	0.07	0.15							
Smoke Point, mm				17.7	11.7							
Flash Point, °F				130	180	240						
Pour Point, °F				<-60	<-55	-40	-5	55				
Freeze Point, °F	-10.8			<-60	<-60							
Basic Nitrogen, Wt %					0.009	0.006	0.003	0.003				
Mercaptan Sulfur, Wt%				<.001	<.001							
Luminometer #				38.0	21.8							
Paraffins, Vol% (GC)		29.29	18.69	8.24	0.26	0	0					
Naphthenes, Vol% (GC)		69.08	66.81	20.41	0.59	0	0					
Aromatics, Vol% (GC)		1.63	8.2	21.19	0.79	0	0					
Olefins, Vol% (FIA)			<1	1	1							
Benzene, Vol%		1.7										
Naphthalenes, Vol%				0.11	0.56							
Pona		Data attached:										
Thermal Stability				FAIL / 4	Too Foamy							
Research Octane #		76.63	56.4	52.66								
Motor Octane #		74.06	56.23	50.02								
Cetane Index				21.8	29.3	32.4	35.1					
Net Heat of Combustion				18350	18220				18400			
Acidity, mg KOH/g	<.01			0.011	<.01				0.004			
Copper Corrosion				1A	1A	1A			1A			
Existent Gum				1.2	3.6	6.8			3.6			
Oxidation Stability				OK-16hrs	OK-16hrs	OK-16hrs			OK-16hrs			
Total Carbon, Wt%	86.85		85.7	86.6	87	87.4	87.5	87.6				
Total Hydrogen, Wt%	13.08		14.1	13.16	12.74	12.38	12.31	12.18				
Total Nitrogen, Wt%	0.006	<.001	<.001	0.002	0.01	0.008	0.006	0.013				
Total Oxygen, Wt%	<.1		<.1	<.1	<.1	<.1	<.1	<.1				
Total Sulfur, Wt%	0.008	0.001	0.001	0.003	0.002	0.003	0.001	0.009				
Kinematic Viscosity, -4 °F				4.12	10.22							
Kinematic Viscosity, 104 °F				1.07	2.042	3.79	7.75					
Kinematic Viscosity, 210 °F					0.754	1.35	2.08	3.52				
Yield												
Weight % Recovered		4.51	24.79	9.04	22.03	14.30	20.80	3.88		0.07	0.17	99.59
Volume % Recovered		5.28	27.14	9.18	21.53	13.55	19.34	3.57		0.10	0.16	99.85
D86 Distillation, temp °F	°F	°F	°F	°F	°F	°F	°F					
IBP	140.3	70.8	169.7	348.6	400	507.5	573.0					
5 ML	214.1	144.1	228.5	359.2	429	510.9	575.4					
10 ML	246.3	147.3	232.5	361.2	424	511.1	576.8					
20 ML	296.7	149.9	237.5	362.3	434	507.0	579.2					
30 ML	354.9	154.5	246.0	363.3	438	510.0	581.3					
40 ML	407.1	157.4	254.1	365.1	441	511.7	583.3					
50 ML	446.7	160.1	264.9	366.9	445	511.8	585.3					
60 ML	489.7	162.8	276.8	368.7	448	511.8	588.0					
70 ML	524.1	165.3	290.4	371.4	456	512.6	594.1					
80 ML	555.8	168.0	304.1	374.5	461	517.6	600.6					
90 ML	592.3	172.0	318.3	379.2	469	522.1	609.9					
95 ML	620.9	175.6	327.0	382.8	480	528.2	621.1					
FINAL VOL.	650.1	198.3	350.7	393.9	490	535.8	626.9					
RECOVERY, Vol%	98.3	98.8	100.3	99.1	98	98.2	99.0					

Sample 8 was produced by combining cuts 1 and 2 in their yield ratios.
Separation was performed using ASTM 2892, 18 plate column.
All test were run using ASTM, UOP or equivalent Conoco Methods.
Thermal Stability: failed tube rating of 4 (highest value)

FIA Test Data	Oil or	1	2	3	4	5	6	7	8 B	Trap	Wash	Yield
Olefins, Vol%			<1	1	1							
Aromatics, Vol%			6	18	29							
Paraffin + Naphthenes, Vol%			94	81	70							

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\002F0201.D
Instrument    : 1                             Vial      :   2
Operator      : Becky Shaver                  Injection :   1
Acquired on   : 21 Jul 95  11:12 AM           Seq. line :   2
Processed on  : 25 Jul 95   2:40 PM
Sample name   : C95029-1
Methodname    : MOD1011.MTH

================================================================
Calculation of RON = 75.70

*** Remark : RON value is out of specified range. ***
Valid range is 94 < Ron < 103
================================================================
       ========================================================
                      REPORT IN WEIGHT %
       ========================================================
       C-num   Naphtenes   Paraffins   Aromatics   Totals
              ==================================================
          3      0.00        0.00        0.00        0.00
          4      0.00        0.00        0.00        0.00
          5      4.04        0.00        0.00        4.04
          6     62.78       22.08        1.68       86.53
          7      4.49        4.81        0.13        9.42
          8      0.00        0.00        0.00        0.00
          9      0.00        0.00        0.00        0.00
         10      0.00        0.00        0.00        0.00
         11      0.00        0.00        0.00        0.00
              ==================================================
       Totals 71.31        26.88        1.80      100.00

                           -------
       Total               100.00


       ========================================================
                      REPORT IN VOLUME %
       ========================================================
       C-num   Naphtenes   Paraffins   Aromatics   Totals
              ==================================================
          3      0.00        0.00        0.00        0.00
          4      0.00        0.00        0.00        0.00
          5      4.01        0.00        0.00        4.01
          6     60.73       24.22        1.52       86.47
          7      4.34        5.07        0.11        9.52
          8      0.00        0.00        0.00        0.00
          9      0.00        0.00        0.00        0.00
         10      0.00        0.00        0.00        0.00
         11      0.00        0.00        0.00        0.00
              ==================================================
       Totals 69.08        29.29        1.63      100.00
                           -------
       Total               100.00
```

```
=================================================================
                            PIONA
=================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\003F0301.D
Instrument    : 1                        Vial      :   3
Operator      : Becky Shaver             Injection :   1
Acquired on   : 21 Jul 95  12:27 PM      Seq. line :   3
Sample name   : 029-2
Methodname    : MOD1011.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0721A.SEQ


=================================================================
Calculation of RON = 79.90

*** Remark : RON value is out of specified range. ***
Valid range is 94 < Ron < 103
=================================================================
   ==============================================================
                    REPORT IN WEIGHT %
   ==============================================================
   C-num  Naphtenes   Paraffins    Aromatics     Totals
          ======================================================
     3      0.00        0.00         0.00          0.00
     4      0.00        0.00         0.00          0.00
     5      0.00        0.00         0.00          0.00
     6      6.29        0.52         0.09          6.90
     7     19.70        4.42         1.83         25.95
     8     18.33        5.07         2.66         26.06
     9     14.77        4.17         4.11         23.05
    10      7.54        2.94         0.00         10.48
    11      0.10        0.31         0.00          0.41
          ======================================================
   Totals 66.74       17.44         8.68         92.85

   PolyNaphthene              7.15
                           -------
   Total                    100.00



   ==============================================================
                    REPORT IN VOLUME %
   ==============================================================
   C-num  Naphtenes   Paraffins    Aromatics     Totals
          ======================================================
     3      0.00        0.00         0.00          0.00
     4      0.00        0.00         0.00          0.00
     5      0.00        0.00         0.00          0.00
     6      6.40        0.60         0.09          7.09
     7     20.04        4.91         1.74         26.70
     8     18.41        5.46         2.51         26.38
     9     14.63        4.38         3.85         22.86
    10      7.24        3.02         0.00         10.26
    11      0.09        0.32         0.00          0.41
          ======================================================
```

```
Totals 66.81          18.69          8.20          93.70

PolyNaphthene              6.30
                        -------
Total                    100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\004F0401.D
Instrument    : 1                          Vial      :   4
Operator      : Becky Shaver               Injection :   1
Acquired on   : 21 Jul 95  01:41 PM        Seq. line :   4
Sample name   : 029-3
Methodname    : MOD1011.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0721A.SEQ

================================================================
Calculation of RON = 99.00

================================================================
   ============================================================
                    REPORT IN WEIGHT %
   ============================================================
C-num   Naphtenes    Paraffins    Aromatics    Totals
        ====================================================
   3       0.00         0.00         0.00         0.00
   4       0.00         0.00         0.00         0.00
   5       0.00         0.00         0.00         0.00
   6       0.00         0.00         0.00         0.00
   7       0.00         0.00         0.00         0.00
   8       0.00         0.00         0.00         0.00
   9       0.95         0.00         6.21         7.15
  10       8.21         0.89        11.95        21.05
  11      10.67         6.67         2.79        20.14
        ====================================================
Totals  19.83          7.56        20.95        48.34

>200                        21.06
PolyNaphthene               30.59
                            -------
Total                      100.00


   ============================================================
                    REPORT IN VOLUME %
   ============================================================
C-num   Naphtenes    Paraffins    Aromatics    Totals
        ====================================================
   3       0.00         0.00         0.00         0.00
   4       0.00         0.00         0.00         0.00
   5       0.00         0.00         0.00         0.00
   6       0.00         0.00         0.00         0.00
   7       0.00         0.00         0.00         0.00
   8       0.00         0.00         0.00         0.00
   9       1.01         0.00         6.29         7.31
  10       8.52         0.99        12.02        21.53
  11      10.88         7.25         2.87        21.00
        ====================================================
Totals  20.41          8.24        21.19        49.83
```

```
>200                    21.05
PolyNaphthene           29.12
                       -------
Total                   100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\005F0501.D
Instrument    : 1                        Vial      :   5
Operator      : Becky Shaver             Injection :   1
Acquired on   : 21 Jul 95  02:56 PM      Seq. line :   5
Sample name   : 029-4
Methodname    : MOD1013.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0721A.SEQ
```

```
==========================================================
                  REPORT IN WEIGHT %
==========================================================
C-num   Naphtenes   Paraffins   Aromatics    Totals
       =================================================
  3      0.00        0.00        0.00         0.00
  4      0.00        0.00        0.00         0.00
  5      0.00        0.00        0.00         0.00
  6      0.00        0.00        0.00         0.00
  7      0.00        0.00        0.00         0.00
  8      0.00        0.00        0.00         0.00
  9      0.00        0.00        0.00         0.00
 10      0.06        0.00        0.78         0.84
 11      0.52        0.24        0.00         0.76
       =================================================
Totals   0.58        0.24        0.78         1.60

>200                          96.52
PolyNaphthene                  1.88
                             -------
Total                        100.00
```
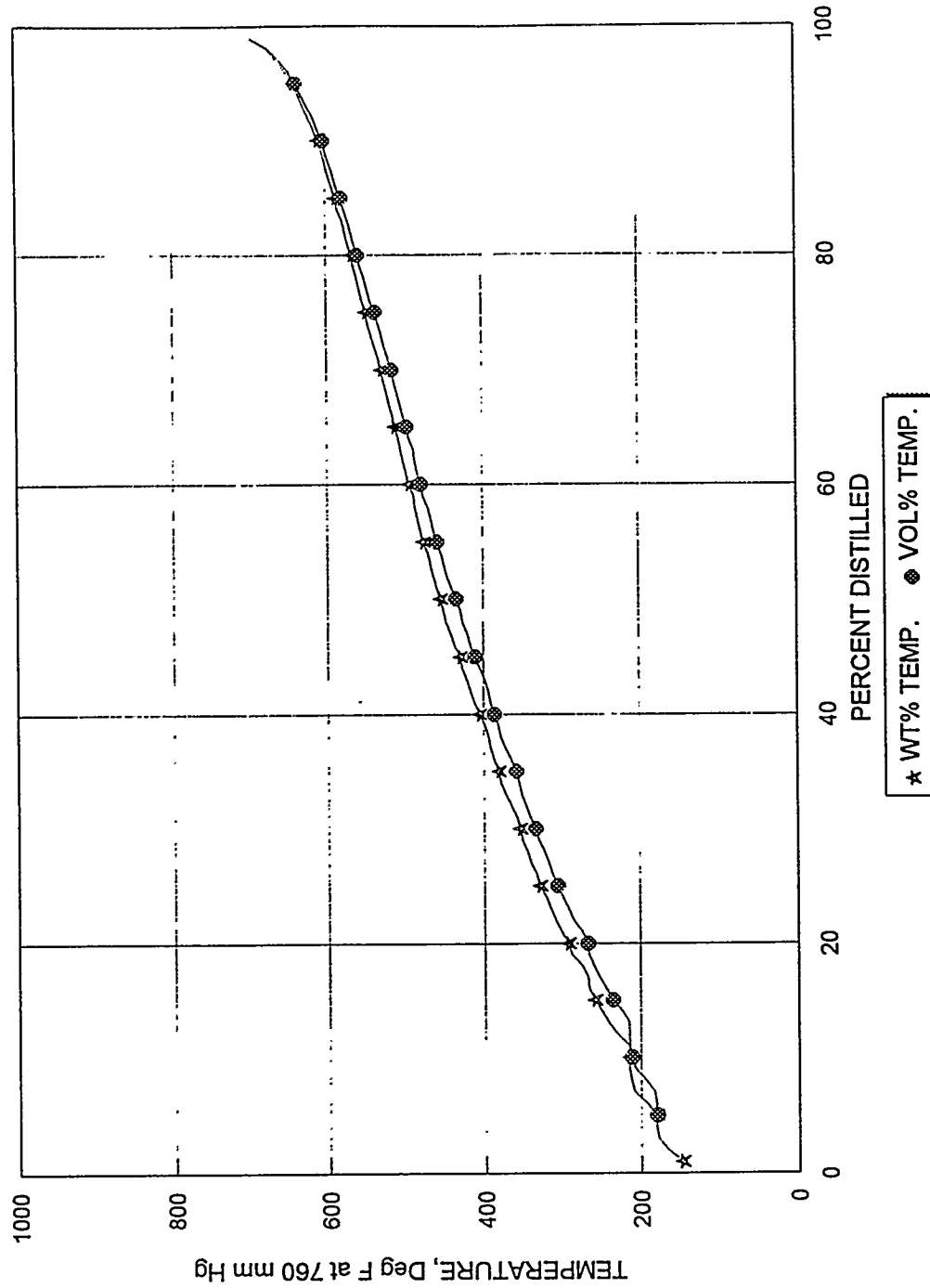
```
==========================================================
                  REPORT IN VOLUME %
==========================================================
C-num   Naphtenes   Paraffins   Aromatics    Totals
       =================================================
  3      0.00        0.00        0.00         0.00
  4      0.00        0.00        0.00         0.00
  5      0.00        0.00        0.00         0.00
  6      0.00        0.00        0.00         0.00
  7      0.00        0.00        0.00         0.00
  8      0.00        0.00        0.00         0.00
  9      0.00        0.00        0.00         0.00
 10      0.06        0.00        0.79         0.85
 11      0.54        0.26        0.00         0.79
       =================================================
Totals   0.59        0.26        0.79         1.65

>200                          96.56
PolyNaphthene                  1.80
                             -------
Total                        100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\006F0601.D
Instrument    : 1                        Vial       :    6
Operator      : Becky Shaver             Injection  :    1
Acquired on   : 21 Jul 95  04:11 PM      Seq. line  :    6
Sample name   : 029-5
Methodname    : MOD1013.MTH
Sequencename  : C:\HPCHEM\1\SEQUENCE\P0721A.SEQ


      ==========================================================
                      REPORT IN WEIGHT %
      ==========================================================
      C-num  Naphtenes   Paraffins   Aromatics    Totals
            ==========================================================
         3     0.00        0.00        0.00         0.00
         4     0.00        0.00        0.00         0.00
         5     0.00        0.00        0.00         0.00
         6     0.00        0.00        0.00         0.00
         7     0.00        0.00        0.00         0.00
         8     0.00        0.00        0.00         0.00
         9     0.00        0.00        0.00         0.00
        10     0.00        0.00        0.00         0.00
        11     0.00        0.00        0.00         0.00
            ==========================================================
      Totals  0.00        0.00        0.00         0.00

      >200                           100.00
                                     -------
      Total                          100.00



      ============================================================
                      REPORT IN VOLUME %
      ============================================================
      C-num  Naphtenes   Paraffins   Aromatics    Totals
            ==========================================================
         3     0.00        0.00        0.00         0.00
         4     0.00        0.00        0.00         0.00
         5     0.00        0.00        0.00         0.00
         6     0.00        0.00        0.00         0.00
         7     0.00        0.00        0.00         0.00
         8     0.00        0.00        0.00         0.00
         9     0.00        0.00        0.00         0.00
        10     0.00        0.00        0.00         0.00
        11     0.00        0.00        0.00         0.00
            ==========================================================
      Totals  0.00        0.00        0.00         0.00

      >200                           100.00
                                     -------
      Total                          100.00
```

```
================================================================
                            PIONA
================================================================
Data File Name: C:\HPCHEM\1\DATA\P0721A\007F0701.D
Instrument     : 1                          Vial      :    7
Operator       : Becky Shaver               Injection :    1
Acquired on    : 21 Jul 95  05:25 PM        Seq. line :    7
Sample name    : 029-6
Methodname     : MOD1013.MTH
Sequencename   : C:\HPCHEM\1\SEQUENCE\P0721A.SEQ

        ========================================================
                      REPORT IN WEIGHT %
        ========================================================
        C-num  Naphtenes  Paraffins   Aromatics   Totals
        ========================================================
           3     0.00        0.00        0.00        0.00
           4     0.00        0.00        0.00        0.00
           5     0.00        0.00        0.00        0.00
           6     0.00        0.00        0.00        0.00
           7     0.00        0.00        0.00        0.00
           8     0.00        0.00        0.00        0.00
           9     0.00        0.00        0.00        0.00
          10     0.00        0.00        0.00        0.00
          11     0.00        0.00        0.00        0.00
        ========================================================
        Totals   0.00        0.00        0.00        0.00

        >200                  100.00
                             -------
        Total                 100.00


        ========================================================
                      REPORT IN VOLUME %
        ========================================================
        C-num  Naphtenes  Paraffins   Aromatics   Totals
        ========================================================
           3     0.00        0.00        0.00        0.00
           4     0.00        0.00        0.00        0.00
           5     0.00        0.00        0.00        0.00
           6     0.00        0.00        0.00        0.00
           7     0.00        0.00        0.00        0.00
           8     0.00        0.00        0.00        0.00
           9     0.00        0.00        0.00        0.00
          10     0.00        0.00        0.00        0.00
          11     0.00        0.00        0.00        0.00
        ========================================================
        Totals   0.00        0.00        0.00        0.00

        >200                  100.00
                             -------
        Total                 100.00
```

HRIPOC-2

TRUE BOILING POINT DISTILLATION CURVE
SIMULATED BY GC

★ WT% TEMP. ● VOL% TEMP.

PERCENT DISTILLED

TEMPERATURE, Deg F at 760 mm Hg

HRIPOC-2

Percent	Wt. % Temp.	Vol. % Temp
1	147	0
5	180	179
10	214	211
15	259	236
20	293	268
25	329	306
30	354	334
35	381	359
40	406	387
45	430	411
50	455	436
55	477	460
60	495	480
65	513	498
70	531	517
75	550	538
80	568	560
85	588	581
90	610	604
95	642	639
100	NA	NA

Initial Boiling Pt °F   140
Final Boiling Pt °F   721
Total Percent off   99.5%

DUPONT

Analysis Report

To   O. K. Cabbiness

From   A.W. Buchholz Jr., CCAS, PCL

Phone   DuCom 442-5708

Subject (Sample Description)   Heat of Combustion Data

Analysis Codes G-BTU, N-BTU	Sample Numbers	Analytical Numbers	Reference Numbers
Charge Number 7003-0000-T002	C95028-3 C95028-4 C95029-3 C95029-4 C95029-8 C95029-8A	7391	AWB A400-60
Method LECO oxygen bomb calorimetry			
Reviewed by: A.W. Buchholz Jr.			

The samples were combusted using a LECO AC-300 oxygen bomb calorimeter which was calibrated using benzoic acid. No combustion aids were needed for the analyses. The condensed combustion products were rinsed from the combustion vessel and titrated for acid formation. Only a small amount of acid was titrated which was probably formed from the nitrogen in the air trapped inside the bomb. A small correction was made for the formation of nitric acid. Corrections for the combustion of the fuse wire were also made.

Water originally in the sample and the water formed in the combusiton reaction are both assumed to vaporize and then condense during the analysis releasing the heat of water vaporization back to the system. The gross heats of combustion or high heating values reported here include the heat released during condensation of the water vapor. The net heat of combustion or low heating values account for the loss of the water heat of vaporization. The net values more closely approximate the heat available to a boiler when a fuel is burned where the water vapor escapes through a flue and the heat of vaporization is not recovered.

Thanks.

A.W. Buchholz Jr.
Sr. Research Chemist

Corporate Center for Analytical Sciences (CCAS), Ponca City Laboratories
P.O. Box 1267, Ponca City, OK 74602-1267

GROSS AND NET HEATS OF COMBUSTION VALUES

SAMPLE NO.	GROSS HEAT OF COMBUSTION G-BTU (BTU/LB)	AVERAGE G-BTU (BTU/LB)	NET HEAT OF COMBUSTION N-BTU (BTU/LB)	AVERAGE N-BTU (BTU/LB)
C95028-3	19,280 19,270	19,280	18,130 18,120	18,120
C95028-4	19,130 19,120	19,130	18,020 18,020	18,020
C95028-8	19,510 19,500	19,510	18,250 18,240	18,250
C95029-3	19,570 19,540	19,550	18,370 18,340	18,350
C95029-4	19,380 19,390	19,380	18,220 18,230	18,220
C95029-8B	19,700 19,670	19,690	18,410 18,380	18,400

Corporate Center for Analytical Sciences (CCAS), Ponca City Laboratories
P.O. Box 1267, Ponca City, OK 74602-1267

Phillips Technology Services
Facilities for Research, Development and Manufacturing

Fuel Octane Testing

January 27, 1995
Kok-6-95

Dale K. Cabbiness
Director, Analytical Services Section
Conoco, Inc.
1000 S. Pine
Ponca City, OK 74603

Dear Dale:

You had asked for a brochure or report concerning Phillips' capability for determining octane number by engine testing using small quantities of fuel. Attached is a description of our Knock Engine Automation System (KEAS) technology that makes it possible to use smaller quantities of fuel, and that also improves the quality of test data.

If you have additional technical questions you can direct them to Vance Kopp at (918) 661-9476. We are considering licensing the KEAS technology. If you would like to know more about this option, please contact Delmar Johnson at (918) 661-0620.

Cordially yours,

Fritz C. Kokesh
Director, Technology Acquisition

Attachment

Phillips Corporate Technology
Phillips Petroleum Company
130 RF PRC
Bartlesville, OK 74004

918-661-3407
918-661-7353 (fax)

Knock Engine Automation System
KEAS

Ver 2.1

Knock Engine Automation System Summary

The KEAS system was developed in the 1980's. It was used initially to determine octane on small quantity samples. The KEAS system utilizes a 80486 IBM AT compatible computer with data acquisition hardware and software. The result is a PC-based control system for the knock engine. The software allows the operator to access the data acquisition capabilities of the computer through user-friendly graphical interfaces. On-line help is available throughout the program. Training of knock engine operators is dramatically simplified and reduced when utilizing this system. This allows refinery operations or other personnel to operate the engines, if necessary. In addition, the KEAS system is easily interfaced to laboratory information systems or local area networks, which facilitates the electronic transfer of data to refinery personnel or databases.

The KEAS system requires about 6 minutes to complete an octane test. It will run two octanes in 8 minutes and duplicates on two samples in 15 minutes. A single determination using standard ASTM procedure takes approximately 30 minutes. The repeatability of this test method should meet or exceed that of the standard ASTM method. The reproducibility of this method is currently under investigation.

The KEAS system is designed to allow the operator to select the mode of operation. It can be used in a fully automatic configuration or the KEAS system can be bypassed and the engine will operate in the standard mode as specified by the test method. The system also allows the operator to monitor critical engine parameters during the test and notifies the operator of an unusual condition.

If you would like further information or a demonstration of the system, please contact your Phillips representative.

Knock Engine Automation System
KEAS

- 50 ml Sample Volume

- Reduced sample turnaround

- Increased sampling frequency

- Interfaces with existing engines and LIMS

PHILLIPS 66

Test methods user for Assay:

Conoco Sample Number: C95028

Conoco Sample Number: C95029

Consol Sample Number: FL2236 - POC-1

Consol Sample Number: FL2364 - POC-2

Test Required	Method used:
API Gravity	ASTM D 4052
Specific Gravity	ASTM D 4052
Aniline Point, °F	ASTM D 611
Concarb, Wt%	ASTM D 4530
Metals: ppm	
Vanadium	Ash and ICP
Nickel	Ash and ICP
Iron	Ash and ICP
Copper	Ash and ICP
Zinc	Ash and ICP
Ash, Wt%	ASTM D 482
RVP	ASTM D 323
Smoke Point, °F	ASTM D 1322
Flash Point, °F	ASTM D 56 and D 93
Pour Point, °F	ASTM D 97
Freeze Point, °F	ASTM D 2386
Basic Nitrogen, Wt %	UOP 269 - 90
Mercaptan Sulfur, Wt%	UOP 163-59 / ASTM D 3227
Luminometer #	ASTM D 1740
Paraffins, Vol%	Analytical Controls Method
Naphthenes, Vol%	Analytical Controls Method
Aromatics, Vol%	Analytical Controls Method
Olefins, Vol%	ASTM D1319
Benzene, Vol%	Analytical Controls Method
Naphthalene, Wt%	ASTM D 1840
Pona	Analytical Controls Method
Thermal Stability	ASTM D 3241
Research Octane #	Phillips Technology Services, KEAS
Motor Octane #	Phillips Technology Services, KEAS
Cetane Index	ASTM D 976
Net Heat of Combustion	ASTM D 4529
Acidity, mg KOH/g	ASTM D 974
Copper Corrosion	ASTM D 130
Existent Gum	ASTM D 381
Oxidation Stability	ASTM D 525
Total Carbon, Wt%	Combustion using Leco CHNS - 932
Total Hydrogen, Wt%	Combustion using Leco CHNS - 932
Total Nitrogen, Wt%	ASTM D 4629
Total Oxygen, Wt%	Combustion using Leco RO - 478
Total Sulfur, Wt%	ASTM 4294
Kinematic Viscosity, -4 °F	ASTM D 445
Kinematic Viscosity, 104 °	ASTM D 445
Kinematic Viscosity, 210 °	ASTM D 445
Yield	ASTM D 2892
Weight % Recovered	ASTM D 2892
Volume % Recovered	ASTM D 2892
D86 Distillation, temp °F	ASTM D 86

APPENDIX 5

CP/MAS ^{13}C-NMR ANALYSES
OF 15 COAL-DERIVED RESID SAMPLES

September 8, 1995

Dr. Sue D. Brandes
Sr. Research Engineer
CONSOL, Inc.
4000 Brownsville Rd.
Library, PA 15129-9566

Dear Dr. Brandes:

We have completed NMR analyses on the fifteen samples of resid composites from various coal liquefaction runs at Wilsonville and HRI. As per our statement of work, we are providing CONSOL with:

     1. Structural and molecular parameters derived from cross polarization and dipolar dephasing NMR measurements following the procedure of Solum et al. (Energy and Fuels 1989, 3, 187). A summary table for the fifteen samples is enclosed.

     2. Data sheets summarizing the spectral data used in the calculations. In all cases, we dropped the last four data points of the dipolar dephasing curves because these data were affected by rotational modulation. Computer fits of the dipolar dephasing data are also enclosed.

     3. A sample calculation using the data from sample #2. We use a slightly different nomenclature for some of the parameters than does the Utah group, so we are enclosing a set of equations showing the comparisons. I hope this is not confusing.

     4. Publication quality copies of the cross polarization NMR spectra for each of the fifteen samples. An additional spectrum is included for sample #1 that includes the instrumental parameters.

I hope everything is in order and that the data are useful to CONSOL in understanding some of the chemistry of coal liquefaction. If you have any questions you can call me at (307) 721-2307.

Sincerely,

Francis P. Miknis
Senior Staff Research Scientist

Carbon Structural Parameters Determined by ^{13}C-NMR

WRI Equations	Descriptor	Utah Equations

(1) $f_{ar} = \dfrac{A_{90-240}}{A_{90-240} + A_{0-90}}$ 　　fraction total sp^2 carbon　　 $f_a = \dfrac{I_{90-240}}{I_{0-240}}$

(2) $f_{CO} = f_a \times \dfrac{A_{165-240}}{A_{90-240}}$ 　　carbonyl fraction　　 $f_a^C = f_a \times \dfrac{I_{165-240}}{I_{90-240}}$

(3) $f_{ar}' = f_{ar} - f_{CO}$ 　　aromatic fraction　　 $f_a' = f_a - f_a^C$

(4) $f_{ar}^{CH} = \dfrac{M_o^{CH}}{M_o^{CH} + M_o^C}$ 　　protonated aromatic fraction including carbonyls, if present.

(5) $f_{ar}^C = \dfrac{M_o^C}{M_o^{CH} + M_o^C}$ 　　nonprotonated aromatic fraction including carbonyls, if present.

(6) $f_{ar}^P = f_{ar}' \times \dfrac{A_{150-165}}{A_{90-165}}$ 　　phenolic substituded fraction　　 $f_a^P = f_a' \times \dfrac{I_{150-165}}{I_{90-165}}$

(7) $f_{ar}^S = f_{ar}' \times \dfrac{A_{135-150}}{A_{90-165}}$ 　　alkylated aromatic fraction　　 $f_a^S = f_a' \times \dfrac{I_{135-150}}{I_{90-165}}$

(8) $f_{ar}^{CH'} = f_{ar}' \times f_{ar}^{CH}$ 　　protonated aromatic fraction corrected for carbonyls　　 $f_a^H = f_a' \times M_p$

(9) $f_{ar}^{C'} = f_{ar}' \times f_{ar}^C$ 　　nonprotonated aromatic fraction corrected for carbonyls　　 $f_a^N = f_a' - f_a^H$

(10) $f_{ar}^B = f_{ar}^{C'} - f_{ar}^P - f_{ar}^S$ 　　aromatic bridgehead fraction　　 $f_a^B = f_a^N - f_a^P - f_a^S$

(11) $f_{ar}^{SP} = \dfrac{f_{ar}^S + f_{ar}^P}{f_{ar}'}$ 　　fraction substituted aromatic carbons　　 $\dfrac{f_a^S + f_a^P}{f_a'}$

(12) $f_{al} = 1 - f_{ar}$ 　　fraction of total sp^3 carbon　　 $f_{al} = 1 - f_a$

Carbon Structural Parameters Determined by ^{13}C-NMR
(con't)

WRI Equations	Descriptor	Utah Equations
(13) $f_{al}^{CH3OCH3} = f_{al} \times \dfrac{A_{0-25} + A_{50-60}}{A_{0-90}}$	methyl and methoxy carbon	$f_{al}^{*} = f_{al} \times \dfrac{I_{2-22} + I_{50-60}}{I_{2-90}}$
(14) $f_{al}^{CHCH2} = f_{al} - f_{al}^{CH3OCH3}$	CH and CH$_2$ carbon fractions	$f_{al}^{H} = f_{al} - f_{al}^{*}$
(15) $f_{al}^{CO} = f_{al}^{CH3OCH3} \times \dfrac{A_{50-90}}{A_{0-90}}$	fraction aliphatic carbons bonded to oxygen	$f_{al}^{O} = f_{al} \times \dfrac{I_{50-90}}{I_{2-90}}$

Equations for Lattice Parameters Determined by ^{13}C-NMR

WRI Equations	Descriptor	Utah Equations

(1) $\quad X_b = \dfrac{f_{ar}}{f_{ar}'}^B$ $\qquad$ mole fraction condensed carbons $\qquad$ $X_b = \dfrac{f_a}{f_a'}^B$

(2) $\quad X_b = \dfrac{1}{2} \times \left[1 - \tanh\left(\dfrac{C_{ar} - 19.21}{4.15} \right) \right] \times X_b' + \dfrac{1}{2} \times \left[1 + \tanh\left(\dfrac{C_{ar} - 19.21}{4.15} \right) \right] \times X_b''$

$\qquad$ C_{ar} $\qquad$ aromatic carbons per cluster $\qquad$ $\dfrac{AC}{CL}$ or C

(3) $\quad X_b' = \dfrac{1}{2} - \dfrac{3}{C_{ar}}$

(4) $\quad X_b'' = 1 - \sqrt{\dfrac{6}{C_{ar}}}$

(5) $\quad \sigma + 1 = \left(f_{ar}^S + f_{ar}^P \right) \times \dfrac{C_{ar}}{f_{ar}'}$ $\qquad$ attachments per cluster

(6) $\quad P_o = \dfrac{f_{ar}^P + f_{ar}^S - f_{al}^{CH3OCH3}}{f_{ar}^P + f_{ar}^S}$ $\qquad$ fraction of intact bridges $\qquad$ $P_o = \dfrac{f_a^P + f_a^S - f_{al}^\bullet}{f_a^P + f_r^S}$

(7) $\quad BL = (\sigma + 1) \times P_o$ $\qquad$ number of bridges and loops $\qquad$ same

(8) $\quad SC = (\sigma + 1) - BL$ $\qquad$ side chains per cluster $\qquad$ same

(9) $\quad MW_c = \dfrac{1201 \times C_{ar}}{f_{ar}' \times \%C}$ $\qquad$ total molecular weight $\qquad$ $MW_c = \dfrac{12.01 \times C}{f_{ar}' \times \%C/100}$

(10) $\quad C_{al} = \dfrac{\%C \times MW_c \times f_{al}}{1201}$ $\qquad$ aliphatic carbon

(11) $\quad M_\delta = \dfrac{\left[MW_c - \dfrac{12 f_{ar}^{C'} C_{ar} - 13 f_{ar}^{CH'}}{f_{ar}^{C''} + f_{ar}^{CH'}} \right]}{\sigma + 1}$ $\qquad$ molecular weight attachment $\qquad$ same

Equations 2-4 were taken from M.S. Solum, R.J. Pugmire and D.M. Grant's article in *Energy and Fuels* 1989, 3, pp.187-193, with slight change in notation.

Solid State ^{13}C NMR Analysis for 15 Resid Composite Samples

Coal	Pittsburgh			WyoDak			Illinois #6			
Run #	Wilsonville259	Wilsonville259	Wilsonville259	Wilsonville260	Wilsonville260	Wilsonville260	Wilsonville261	Wilsonville261	Wilsonville261	Wilsonville261
Location	V-1067	R-1235	V-131B	V-1067	R-1235	V-131B	V-1067	V-1067	R-1235	V-131B
Sample #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	7 (repeat)	8.000	9.000
%C	90.240	90.120	91.010	91.030	90.890	91.030	89.300	89.300	88.360	88.920
M_o^{CH}	0.437	0.449	0.341	0.340	0.397	0.380	0.473	0.504	0.475	0.361
M_o^C	0.563	0.551	0.659	0.660	0.603	0.620	0.527	0.496	0.525	0.639
f_{ar}	0.717	0.757	0.703	0.805	0.807	0.780	0.684	0.712	0.693	0.665
f_{al}	0.283	0.243	0.297	0.195	0.193	0.220	0.316	0.288	0.307	0.335
f_{ar}'	0.710	0.750	0.694	0.764	0.768	0.757	0.682	0.709	0.680	0.661
f_{co}	0.008	0.006	0.008	0.041	0.040	0.023	0.002	0.003	0.014	0.004
f_{ar}^P	0.043	0.034	0.033	0.073	0.081	0.061	0.028	0.021	0.046	0.028
f_{ar}^S	0.170	0.172	0.185	0.233	0.238	0.224	0.191	0.163	0.186	0.169
$f_{al}^{CH3OCH3}$	0.108	0.107	0.122	0.097	0.089	0.109	0.132	0.128	0.115	0.135
f_{al}^{CHCH2}	0.175	0.137	0.176	0.098	0.103	0.111	0.184	0.159	0.192	0.200
f_{al}^{OO}	0.001	0.003	0.009	0.003	0.006	0.005	0.005	0.002	0.009	0.006
f_{ar}^{CH}	0.437	0.449	0.341	0.340	0.397	0.380	0.473	0.504	0.475	0.361
f_{ar}^C	0.563	0.551	0.659	0.660	0.603	0.620	0.527	0.496	0.525	0.639
$f_{ar}^{CH'}$	0.310	0.337	0.236	0.260	0.305	0.288	0.323	0.357	0.323	0.239
$f_{ar}^{C'}$	0.400	0.414	0.458	0.505	0.463	0.469	0.359	0.351	0.357	0.423
f_{ar}^B	0.187	0.208	0.240	0.200	0.144	0.184	0.141	0.168	0.125	0.225
f_{ar}^{SP}	0.299	0.274	0.314	0.399	0.415	0.376	0.321	0.259	0.341	0.299
X_b	0.264	0.277	0.345	0.261	0.188	0.244	0.206	0.237	0.184	0.340
X_b'	0.262	0.274	0.324	0.259	0.188	0.242	0.206	0.236	0.183	0.321
C_{ar}	12.596	13.292	17.029	12.469	9.604	11.613	10.212	11.345	9.477	16.797
X_b^u	0.310	0.328	0.406	0.306	0.210	0.281	0.233	0.273	0.204	0.402
sigma+1	3.769	3.645	5.349	4.977	3.983	4.371	3.274	2.941	3.236	5.016
P_o	0.493	0.481	0.442	0.683	0.719	0.617	0.395	0.301	0.504	0.317
BL	1.859	1.753	2.367	3.397	2.864	2.699	1.293	0.886	1.632	1.588
SC	1.910	1.892	2.983	1.579	1.119	1.672	1.980	2.055	1.605	3.428
MW_c	236.215	236.106	323.734	215.253	165.344	202.462	201.347	215.290	189.537	342.968
Cal	5.02	4.813	7.297	3.175	2.413	3.373	4.728	4.608	4.277	8.505
M_δ	21.110	19.379	21.234	12.334	11.619	13.426	22.594	24.965	22.035	26.982

V-1067 = Second Stage , R-1235 = Interstage , V-131B = Recycle Stage

Solid State ^{13}C NMR Analysis for 15 Resid Composite Samples

Coal	Wilsonville262	Wilsonville262	Black Thunder Wilsonville262	Wilsonville262	Wilsonville258	Illinois # 6	BlackThunder
Run # / Location	V-1067	R-1235	R-1235	V-131B	V-131B	HRI POC-1 O-43	HRI POC-2 O-43
Sample #	10	11	11 (repeat)	12	13	14	15
%C	90.39	89.07	89.07	89.55	90.34	89.06	91.76
M_o^{CH}	0.390	0.304	0.383	0.484	0.412	0.340	0.490
M_o^{C}	0.610	0.696	0.617	0.516	0.588	0.660	0.509
f_{ar}	0.677	0.723	0.736	0.706	0.758	0.609	0.563
f_{al}	0.323	0.277	0.264	0.294	0.242	0.391	0.437
f_{al}'	0.657	0.710	0.732	0.702	0.744	0.605	0.556
f_{co}	0.021	0.012	0.004	0.005	0.014	0.004	0.007
f_{ar}^{P}	0.054	0.056	0.046	0.047	0.054	0.018	0.019
f_{ar}^{S}	0.193	0.208	0.199	0.204	0.209	0.154	0.133
$f_{al}^{CH3OCH3}$	0.158	0.139	0.120	0.118	0.130	0.147	0.156
f_{al}^{CHCH2}	0.165	0.139	0.144	0.175	0.112	0.244	0.281
f_{al}^{CO}	0.008	0.004	0.004	0.008	0.009	0.007	0.009
f_{ar}^{CH}	0.390	0.304	0.383	0.484	0.412	0.340	0.490
f_{ar}^{C}	0.610	0.696	0.617	0.516	0.588	0.660	0.510
$f_{ar}^{CH'}$	0.256	0.216	0.280	0.340	0.306	0.205	0.272
$f_{ar}^{C'}$	0.400	0.494	0.452	0.362	0.438	0.399	0.283
f_{ar}^{B}	0.153	0.230	0.207	0.111	0.175	0.227	0.131
f_{ar}^{SP}	0.376	0.372	0.335	0.357	0.353	0.284	0.273
X_b	0.233	0.324	0.282	0.159	0.235	0.376	0.237
X_b'	0.233	0.310	0.279	0.159	0.233	0.337	0.237
C_{ar}	11.227	15.828	13.554	8.787	11.236	18.456	11.387
X_b''	0.269	0.384	0.335	0.174	0.269	0.430	0.274
sigma+1	4.226	5.891	4.540	3.137	3.972	5.248	3.112
P_o	0.362	0.474	0.510	0.527	0.506	0.144	-0.025
BL	1.528	2.795	2.318	1.654	2.011	0.755	-0.077
SC	2.697	3.096	2.222	1.483	1.961	4.492	3.189
MW_c	227.116	300.419	249.746	167.925	200.692	411.676	268.188
C_{al}	5.513	6.182	4.886	3.676	3.647	11.950	8.956
M_b	20.828	17.939	18.041	18.559	15.415	35.050	40.480

V-1067 = Second Stage, R-1235 = Interstage, V-131B = Recycle Stage

Sample: CONSOL 1

Integration of ^{13}C CP Spectrum

A_{0-90}	65.9000	f_{ar}	0.7174
A_{90-240}	167.3000	f_{al}	0.2826
$A_{165-240}$	1.8000	f_{ar}'	0.7097
$A_{150-165}$	10.0000	f_{CO}	0.0077
A_{90-165}	166.1000	f_{ar}^{P}	0.0427
$A_{135-150}$	39.7000	f_{ar}^{S}	0.1696
A_{0-25}	22.1000	$f_{al}^{CH3OCH3}$	0.1076
A_{50-60}	3.0000	f_{al}^{CHCH2}	0.1750
A_{50-90}	0.4000	f_{al}^{CO}	0.0007
		f_{ar}^{CH}	0.4366
		f_{ar}^{C}	0.5634

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.4366	$f_{ar}^{CH'}$	0.3099
M_o^{C}	0.5634	$f_{ar}^{C'}$	0.3998
T_{dd}^{G}	19.72	f_{ar}^{B}	0.1875
T_{dd}^{L}	210.1	f_{ar}^{SP}	0.2992
		X_b	0.2641
		X_b'	0.2622
		X_b''	0.3103

Elemental Analysis

%C	90.24
%H	6.39
MW	12.01
$(H/C)_T$	0.8504

Structural Parameters:

C_{ar}	12.615
C_{al}	5.023
sigma+1	3.775
P_o	0.4931
BL	1.861
SC	1.913
MW_c	236.5654
M_δ	21.1101

Comments: 8/7/95   Sample: Wil. 259; V-1067

Dir: CONSOL
fn^{dd}: con1.1ddft   Contact: S. Brandes
fn^{cp}: con1.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140, 160, 180 and 200 µsec were excluded from the analysis.

Sample: CONSOL 2

Integration of ^{13}C CP Spectrum

A_{0-90}	53.8000
A_{90-240}	167.2000
$A_{165-240}$	1.4000
$A_{150-165}$	7.5000
A_{90-165}	165.9000
$A_{135-150}$	38.0000
A_{0-25}	22.1000
A_{50-60}	1.5000
A_{50-90}	1.5000

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.4486
M_o^{C}	0.5514
T_{dd}^{G}	17.92
T_{dd}^{L}	202.3

Elemental Analysis

%C	90.12
%H	6.19
MW	12.01
$(H/C)_T$	0.8249

f_{ar}	0.7566
f_{al}	0.2434
f_{ar}'	0.7502
f_{CO}	0.0063
f_{ar}^{P}	0.0339
f_{ar}^{S}	0.1718
$f_{al}^{CH3OCH3}$	0.1068
f_{al}^{CHCH2}	0.1367
f_{al}^{CO}	0.0030
f_{ar}^{CH}	0.4486
f_{ar}^{C}	0.5514
$f_{ar}^{CH'}$	0.3365
$f_{ar}^{C'}$	0.4137
f_{ar}^{B}	0.2079
f_{ar}^{SP}	0.2743
X_b	0.2772
X_b'	0.2742
X_b''	0.3280

Structural Parameters:

C_{ar}	13.287
C_{al}	4.312
sigma+1	3.644
P_o	0.4810
BL	1.753
SC	1.891
MW_c	236.0289
M_δ	19.3792

Sample: CONSOL 3

Integration of ^{13}C CP Spectrum

A_{0-90}	70.7000
A_{90-240}	167.0000
$A_{165-240}$	2.0000
$A_{150-165}$	7.9000
A_{90-165}	164.9000
$A_{135-150}$	43.9000
A_{0-25}	24.9000
A_{50-60}	4.0000
A_{50-90}	5.1000

f_{ar}	0.7026
f_{al}	0.2974
f_{ar}'	0.6942
f_{CO}	0.0084
f_{ar}^P	0.0333
f_{ar}^S	0.1848
$f_{al}^{CH3OCH3}$	0.1216
f_{al}^{CHCH2}	0.1759
f_{al}^{CO}	0.0088
f_{ar}^{CH}	0.3406
f_{ar}^C	0.6594
$f_{ar}^{CH'}$	0.2365
$f_{ar}^{C'}$	0.4577
f_{ar}^B	0.2396
f_{ar}^{SP}	0.3141
X_b	0.3452
X_b'	0.3241
X_b''	0.4069

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.3406
M_o^C	0.6594
T_{dd}^G	20.68
T_{dd}^L	146.9

Elemental Analysis

%C	91.01
%H	6.50
MW	12.01
$(H/C)_T$	0.8578

Structural Parameters

C_{ar}	17.05
C_{al}	7.307
sigma+1	5.36
P_o	0.4424
BL	2.3701
SC	2.9870
MW_c	324.21
M_δ	21.2336

Comments: 8/7/95 Sample: Wil 259;V131B

Dir: CONSOL
fn^{dd}: con3.1ddft   Contact: S. Brandes
fn^{cp}: con3.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 4

Integration of ^{13}C CP Spectrum

		f_{ar}	0.8054
		f_{al}	0.1946
A_{0-90}	40.2000	f_{ar}'	0.7643
A_{90-240}	166.4000	f_{CO}	0.0411
$A_{165-240}$	8.5000	f_{ar}^P	0.0725
$A_{150-165}$	15.0000	f_{ar}^S	0.2325
A_{90-165}	158.1000	$f_{al}^{CH3OCH3}$	0.0968
$A_{135-150}$	48.1000	f_{al}^{CHCH2}	0.0978
A_{0-25}	19.0000	f_{al}^{CO}	0.0026
A_{50-60}	1.0000	f_{ar}^{CH}	0.3397
A_{50-90}	1.1000	f_{ar}^C	0.6603
		$f_{ar}^{CH'}$	0.2597
^{13}C Spectrum Dipolar Dephasing		$f_{ar}^{C'}$	0.5046
M_o^{CH}	0.3398	f_{ar}^B	0.1996
M_o^C	0.6603	f_{ar}^{SP}	0.3991
T_{dd}^G	17.79	X_b	0.2611
T_{dd}^L	124.6	X_b'	0.2592
		X_b''	0.3061

Elemental Analysis

%C	91.03
%H	6.56
MW	12.01
$(H/C)_T$	0.8655

Structural Parameters

C_{ar}	12.46
C_{al}	3.172
sigma+1	4.97
P_o	0.6826
BL	3.3948
SC	1.5782
MW_c	215.09
M_δ	12.3345

Comments: 8/7/95   Sample: Wil. 260,V1067

Dir: CONSOL
fn^{dd}:   con4.1ddft   Contact: S. Brandes
fn^{cp}:   con4.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 5

Integration of ^{13}C CP Spectrum

A_{0-90}	39.9000	f_{ar}	0.8072
A_{90-240}	167.0000	f_{al}	0.1928
$A_{165-240}$	8.2000	f_{ar}'	0.7675
$A_{150-165}$	16.7000	f_{CO}	0.0396
A_{90-165}	158.9000	f_{ar}^{P}	0.0807
$A_{135-150}$	49.2000	f_{ar}^{S}	0.2376
A_{0-25}	16.0000	$f_{al}^{CH3OCH3}$	0.0894
A_{50-60}	2.5000	f_{al}^{CHCH2}	0.1034
A_{50-90}	2.5000	f_{al}^{CO}	0.0056
		f_{ar}^{CH}	0.3974
		f_{ar}^{C}	0.6026

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.3974	$f_{ar}^{CH'}$	0.3050
M_o^{C}	0.6026	$f_{ar}^{C'}$	0.4625
T_{dd}^{G}	13.41	f_{ar}^{B}	0.1442
T_{dd}^{L}	126.6	f_{ar}^{SP}	0.4147
		X_b	0.1879
		X_b'	0.1883
		X_b''	0.2105

Elemental Analysis

%C	90.89
%H	6.19
MW	12.01
$(H/C)_T$	0.8179

Structural Parameters

C_{ar}	9.63
C_{al}	2.418
sigma+1	3.99
P_o	0.7191
BL	2.8705
SC	1.1213
MW_c	165.71
M_δ	11.6192

Sample: CONSOL 6

Integration of ^{13}C CP Spectrum

A_{0-90}	47.0000	f_{ar}	0.7802
A_{90-240}	166.8000	f_{al}	0.2198
$A_{165-240}$	5.0000	f_{ar}'	0.7568
$A_{150-165}$	12.9000	f_{co}	0.0234
A_{90-165}	161.0000	f_{ar}^{P}	0.0606
$A_{135-150}$	47.7000	f_{ar}^{S}	0.2242
A_{0-25}	21.2000	$f_{al}^{CH3OCH3}$	0.1090
A_{50-60}	2.1000	f_{al}^{CHCH2}	0.1109
A_{50-90}	2.1000	f_{al}^{CO}	0.0049

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.3801	f_{ar}^{CH}	0.3801
M_o^{C}	0.6199	f_{ar}^{C}	0.6199
T_{dd}^{G}	14.32	$f_{ar}^{CH'}$	0.2876
T_{dd}^{L}	130.0	$f_{ar}^{C'}$	0.4692
		f_{ar}^{B}	0.1843
		f_{ar}^{SP}	0.3764

Elemental Analysis

%C	91.03	X_b	0.2435
%H	6.61	X_b'	0.2431
MW	12.01	X_b''	0.2832
$(H/C)_T$	0.8721		

Structural Parameters

C_{ar}	11.68
C_{al}	3.392
sigma+1	4.40
P_o	0.6174
BL	2.7138
SC	1.6816
MW_c	203.58
M_δ	13.4261

Comments: 8/7/95   Sample: Wil. 260,V131B

Dir: CONSOL
fn^{dd}:   con6.1ddft   Contact: S. Brandes
fn^{cp}:   con6.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 7

Integration of ^{13}C CP Spectrum

A_{0-90}	76.4000
A_{90-240}	165.5000
$A_{165-240}$	0.5000
$A_{150-165}$	6.8000
A_{90-165}	165.0000
$A_{135-150}$	46.1000
A_{0-25}	29.1000
A_{50-60}	2.9000
A_{50-90}	2.9000

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.4733
M_o^{C}	0.5267
T_{dd}^{G}	19.09
T_{dd}^{L}	204.5

Elemental Analysis

%C	89.30
%H	6.61
MW	12.01
$(H/C)_T$	0.8890

f_{ar}	0.6842
f_{al}	0.3158
f_{ar}'	0.6821
f_{CO}	0.0021
f_{ar}^{P}	0.0281
f_{ar}^{S}	0.1906
$f_{al}^{CH3OCH3}$	0.1323
f_{al}^{CHCH2}	0.1835
f_{al}^{CO}	0.0050
f_{ar}^{CH}	0.4733
f_{ar}^{C}	0.5267
$f_{ar}^{CH'}$	0.3229
$f_{ar}^{C'}$	0.3592
f_{ar}^{B}	0.1406
f_{ar}^{SP}	0.3206
X_b	0.2061
X_b'	0.2057
X_b''	0.2329

Structural Parameters

C_{ar}	10.20
C_{al}	4.721
sigma+1	3.27
P_o	0.3951
BL	1.2914
SC	1.9772
MW_c	201.02
M_δ	22.5940

Comments: 8/7/95   Sample: Wil. 261.V1067

Dir: CONSOL
fn^{dd}:   con7.1ddft   Contact: S. Brandes
fn^{cp}:   con7.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 7   Run 2

Integration of ^{13}C CP Spectrum

A_{0-90}	67.5000	f_{ar}	0.7122
A_{90-240}	167.0000	f_{al}	0.2878
$A_{165-240}$	0.8000	f_{ar}'	0.7087
$A_{150-165}$	5.0000	f_{CO}	0.0034
A_{90-165}	167.8000	f_{ar}^{P}	0.0211
$A_{135-150}$	38.5000	f_{ar}^{S}	0.1626
A_{0-25}	28.9000	$f_{al}^{CH3OCH3}$	0.1284
A_{50-60}	1.2000	f_{al}^{CHCH2}	0.1595
A_{50-90}	1.2000	f_{al}^{CO}	0.0023

Integration table continued:

f_{ar}^{CH}	0.5042
f_{ar}^{C}	0.4958
$f_{ar}^{CH'}$	0.3573
$f_{ar}^{C'}$	0.3514
f_{ar}^{B}	0.1677
f_{ar}^{SP}	0.2592
X_{b}	0.2366
X_{b}'	0.2356
X_{b}''	0.2728

^{13}C Spectrum Dipolar Dephasing

M_{o}^{CH}	0.5042
M_{o}^{C}	0.4958
T_{dd}^{G}	19.63
T_{dd}^{L}	275.8

Elemental Analysis

%C	89.30
%H	6.61
MW	12.01
$(H/C)_{T}$	0.8890

Structural Parameters

C_{ar}	11.35
C_{al}	4.608
sigma+1	2.94
P_{o}	0.3014
BL	0.8864
SC	2.0547
MW_{c}	215.28
M_{δ}	24.9647

Comments: 8/17/95   Sample: Wil. 261;V1067

Dir:	CONSOL
fn^{dd}:	con7.2ddft
fn^{cp}:	con7.2cp
ct:	2 msec
temp:	23°C

Contact: S. Brandes

Data pts. at 140,160,180 and 200 µsec were excluded from the analysis.

Sample: CONSOL 8

Integration of ^{13}C CP Spectrum

A_{0-90}	74.1000
A_{90-240}	167.5000
$A_{165-240}$	3.3000
$A_{150-165}$	11.0000
A_{90-165}	164.0000
$A_{135-150}$	45.0000
A_{0-25}	23.6000
A_{50-60}	4.2000
A_{50-90}	5.8000

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.4750
M_o^{C}	0.5250
T_{dd}^{G}	17.30
T_{dd}^{L}	242.6

Elemental Analysis

%C	88.36
%H	6.66
MW	12.01
$(H/C)_T$	0.9052

f_{ar}	0.6933
f_{al}	0.3067
f_{ar}'	0.6796
f_{CO}	0.0137
f_{ar}^{P}	0.0456
f_{ar}^{S}	0.1865
$f_{al}^{CH3OCH3}$	0.1151
f_{al}^{CHCH2}	0.1916
f_{al}^{CO}	0.0090
f_{ar}^{CH}	0.4750
f_{ar}^{C}	0.5250
$f_{ar}^{CH'}$	0.3228
$f_{ar}^{C'}$	0.3568
f_{ar}^{B}	0.1247
f_{ar}^{SP}	0.3415
X_b	0.1835
X_b'	0.1836
X_b''	0.2045

Structural Parameters

C_{ar}	9.48
C_{al}	4.279
sigma+1	3.24
P_o	0.5042
BL	1.6322
SC	1.6052
MW_c	189.61
M_δ	22.0349

Comments: 8/8/95   Sample: Wil. 261;R1235

Dir: CONSOL
fn^{dd}:   con8.1ddft   Contact: S. Brandes
fn^{cp}:   con8.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 µsec were excluded from the analysis.

Sample: CONSOL 9

Integration of ^{13}C CP Spectrum			
A_{0-90}	84.1000	f_{ar}	0.6651
A_{90-240}	167.0000	f_{al}	0.3349
$A_{165-240}$	0.9000	f_{ar}'	0.6615
$A_{150-165}$	7.1000	f_{CO}	0.0036
A_{90-165}	166.1000	f_{ar}^{P}	0.0283
$A_{135-150}$	42.5000	f_{ar}^{S}	0.1693
A_{0-25}	31.0000	$f_{al}^{CH3OCH3}$	0.1350
A_{50-60}	2.9000	f_{al}^{CHCH2}	0.1999
A_{50-90}	3.8000	f_{al}^{CO}	0.0061
		f_{ar}^{CH}	0.3613
^{13}C Spectrum Dipolar Dephasing		f_{ar}^{C}	0.6387
M_{o}^{CH}	0.3613	$f_{ar}^{CH'}$	0.2390
M_{o}^{C}	0.6387	$f_{ar}^{C'}$	0.4225
T_{dd}^{G}	18.72	f_{ar}^{B}	0.2250
T_{dd}^{L}	160.8	f_{ar}^{SP}	0.2986
		X_{b}	0.3401
Elemental Analysis		X_{b}'	0.3213
%C	88.92	X_{b}''	0.4021
%H	6.61		
MW	12.01		
$(H/C)_{T}$	0.8928		

Structural Parameters

C_{ar}	16.79
C_{al}	8.499
sigma+1	5.01
P_{o}	0.3165
BL	1.5867
SC	3.4261
MW_{c}	342.76
M_{s}	26.9815

Comments: 8/8/95 Sample: Wil 261;V131B

Dir: CONSOL
fn^{dd}: con9.1ddft   Contact: S. Brandes
fn^{cp}: con9.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 10

Integration of ^{13}C CP Spectrum

A_{0-90}	79.5000
A_{90-240}	167.0000
$A_{165-240}$	5.1000
$A_{150-165}$	13.4000
A_{90-165}	161.8000
$A_{135-150}$	47.5000
A_{0-25}	34.9000
A_{50-60}	4.0000
A_{50-90}	4.0000

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.3903
M_o^{C}	0.6097
T_{dd}^{G}	17.31
T_{dd}^{L}	158.6

Elemental Analysis

%C	90.39
%H	7.09
MW	12.01
$(H/C)_T$	0.9420

f_{ar}	0.6775
f_{al}	0.3225
f_{ar}'	0.6568
f_{CO}	0.0207
f_{ar}^{P}	0.0544
f_{ar}^{S}	0.1928
$f_{al}^{CH3OCH3}$	0.1578
f_{al}^{CHCH2}	0.1647
f_{al}^{CO}	0.0079
f_{ar}^{CH}	0.3903
f_{ar}^{C}	0.6097
$f_{ar}^{CH'}$	0.2563
$f_{ar}^{C'}$	0.4005
f_{ar}^{B}	0.1532
f_{ar}^{SP}	0.3764
X_b	0.2333
X_b'	0.2326
X_b''	0.2687

Structural Parameters

C_{ar}	11.22
C_{al}	5.510
sigma+1	4.22
P_o	0.3616
BL	1.5273
SC	2.6959
MW_c	226.99
M_δ	20.8283

Comments: 8/8/95 Sample: Wil. 262;V1067

Dir: CONSOL
fn^{dd}: con10.1ddft Contact: S. Brandes
fn^{cp}: con10.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 11

Integration of ^{13}C CP Spectrum

A_{0-90}	64.1000	f_{ar}	0.7225
A_{90-240}	166.9000	f_{al}	0.2775
$A_{165-240}$	2.8000	f_{ar}'	0.7104
$A_{150-165}$	13.0000	f_{CO}	0.0121
A_{90-165}	163.9000	f_{ar}^{P}	0.0563
$A_{135-150}$	48.0000	f_{ar}^{S}	0.2080
A_{0-25}	30.1000	$f_{al}^{CH3OCH3}$	0.1390
A_{50-60}	2.0000	f_{al}^{CHCH2}	0.1385
A_{50-90}	2.0000	f_{al}^{CO}	0.0043
		f_{ar}^{CH}	0.3043
		f_{ar}^{C}	0.6957

^{13}C Spectrum Dipolar Dephasing

M_{o}^{CH}	0.3043	$f_{ar}^{CH'}$	0.2162
M_{o}^{C}	0.6957	$f_{ar}^{C'}$	0.4942
T_{dd}^{G}	16.09	f_{ar}^{B}	0.2298
T_{dd}^{L}	127.4	f_{ar}^{SP}	0.3722
		X_{b}	0.3235
		X_{b}'	0.3104
		X_{b}''	0.3843

Elemental Analysis

%C	89.07
%H	6.87
MW	12.01
$(H/C)_{T}$	0.9263

Structural Parameters

C_{ar}	15.83
C_{al}	6.182
sigma+1	5.89
P_{o}	0.4744
BL	2.7944
SC	3.0959
MW_{c}	300.40
M_{δ}	17.9390

Sample: CONSOL 11   Run 2

Integration of ^{13}C CP Spectrum

A_{0-90}	59.8000	f_{ar}	0.7362
A_{90-240}	166.9000	f_{al}	0.2638
$A_{165-240}$	1.0000	f_{ar}'	0.7318
$A_{150-165}$	10.5000	f_{CO}	0.0044
A_{90-165}	166.0000	f_{ar}^{P}	0.0463
$A_{135-150}$	45.1000	f_{ar}^{S}	0.1988
A_{0-25}	26.1000	$f_{al}^{CH3OCH3}$	0.1200
A_{50-60}	1.1000	f_{al}^{CHCH2}	0.1438
A_{50-90}	2.1000	f_{al}^{CO}	0.0042
		f_{ar}^{CH}	0.3829

^{13}C Spectrum Dipolar Dephasing

M_{o}^{CH}	0.3829	f_{ar}^{C}	0.6171
M_{o}^{C}	0.6171	$f_{ar}^{CH'}$	0.2802
T_{dd}^{G}	20.61	$f_{ar}^{C'}$	0.4516
T_{dd}^{L}	173.0	f_{ar}^{B}	0.2065
		f_{ar}^{SP}	0.3349

Elemental Analysis

%C	89.07	X_{b}	0.2822
%H	6.87	X_{b}'	0.2785
MW	12.01	X_{b}''	0.3345
$(H/C)_{T}$	0.9263		

Structural Parameters

C_{ar}	13.55
C_{al}	4.883
sigma+1	4.54
P_{o}	0.5105
BL	2.3163
SC	2.2211
MW_{c}	249.61
M_{δ}	18.0407

Comments: 8/14/95   Sample: Wil. 262;R1235

Dir: CONSOL
fn^{dd}_{x} con11.2ddft   Contact: S. Brandes
fn^{cp}_{x} con11.2cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 12

Integration of ^{13}C CP Spectrum

A_{0-90}	69.4000		
A_{90-240}	167.0000		
$A_{165-240}$	1.1000		
$A_{150-165}$	11.1000		
A_{90-165}	165.8000		
$A_{135-150}$	48.1000		
A_{0-25}	24.0000		
A_{50-60}	4.0000		
A_{50-90}	4.9000		

f_{ar}	0.7064
f_{al}	0.2936
f_{ar}'	0.7018
f_{CO}	0.0047
f_{ar}^{P}	0.0470
f_{ar}^{S}	0.2036
$f_{al}^{CH3OCH3}$	0.1184
f_{al}^{CHCH2}	0.1751
f_{al}^{CO}	0.0084
f_{ar}^{CH}	0.4842
f_{ar}^{C}	0.5158
$f_{ar}^{CH'}$	0.3398
$f_{ar}^{C'}$	0.3620
f_{ar}^{B}	0.1114
f_{ar}^{SP}	0.3571
X_b	0.1587
X_b'	0.1591
X_b''	0.1743

^{13}C Spectrum Dipolar Dephasing

M_o^{CH}	0.4842
M_o^{C}	0.5158
T_{dd}^{G}	21.37
T_{dd}^{L}	327.8

Elemental Analysis

%C	89.55
%H	7.06
MW	12.01
$(H/C)_T$	0.9469

Structural Parameters

C_{ar}	8.80
C_{al}	3.68
sigma+1	3.14
P_o	0.5273
BL	1.6569
SC	1.4853
MW_c	168.18
M_δ	18.5588

Comments: 8/9/95   Sample: Wil. 262 V131B

Dir: CONSOL
fn^{dd}:   con12.1ddft   Contact: S. Brandes
fn^{cp}:   con12.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 13

Integration of ^{13}C CP Spectrum

A_{0-90}	53.2000	f_{ar}	0.7584
A_{90-240}	167.0000	f_{al}	0.2416
$A_{165-240}$	3.1000	f_{ar}'	0.7443
$A_{150-165}$	11.9000	f_{CO}	0.0141
A_{90-165}	163.8000	f_{ar}^{P}	0.0541
$A_{135-150}$	46.0000	f_{ar}^{S}	0.2090
A_{0-25}	25.9000	$f_{al}^{CH3OCH3}$	0.1299
A_{50-60}	2.7000	f_{al}^{CHCH2}	0.1117
A_{50-90}	3.6000	f_{al}^{CO}	0.0088
		f_{ar}^{CH}	0.4118
		f_{ar}^{C}	0.5882

^{13}C Spectrum Dipolar Dephasing

M_{o}^{CH}	0.4118	$f_{ar}^{CH'}$	0.3065
M_{o}^{C}	0.5882	$f_{ar}^{C'}$	0.4378
T_{dd}^{G}	13.74	f_{ar}^{B}	0.1747
T_{dd}^{L}	149.7	f_{ar}^{SP}	0.3535
		X_{b}	0.2347
		X_{b}'	0.2330
		X_{b}''	0.2693

Elemental Analysis

%C	90.34
%H	8.55
MW	12.01
$(H/C)_{T}$	1.1367

Structural Parameters

C_{ar}	11.24
C_{al}	3.65
sigma+1	3.97
P_{o}	0.5063
BL	2.0113
SC	1.9609
MW_{c}	200.71
M_{δ}	15.4154

Comments: 8/10/95   Sample: Wil. 258;V131B

Dir: CONSOL
fn^{dd}:   con13.1ddft   Contact: S. Brandes
fn^{cp}:   con13.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140,160,180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 14

Integration of ^{13}C CP Spectrum

		f_{ar}	0.6086
		f_{al}	0.3914
A_{0-90}	108.0000	f_{ar}'	0.6046
A_{90-240}	167.9000	f_{CO}	0.0040
$A_{165-240}$	1.1000	f_{ar}^{P}	0.0178
$A_{150-165}$	4.9000	f_{ar}^{S}	0.1541
A_{90-165}	166.0000	$f_{al}^{CH3OCH3}$	0.1472
$A_{135-150}$	42.3000	f_{al}^{CHCH2}	0.2443
A_{0-25}	36.5000	f_{al}^{CO}	0.0068
A_{50-60}	4.1000	f_{ar}^{CH}	0.3398
A_{50-90}	5.0000	f_{ar}^{C}	0.6602
		$f_{ar}^{CH'}$	0.2054
		$f_{ar}^{C'}$	0.3992

^{13}C Spectrum Dipolar Dephasing

M_{o}^{CH}	0.3398	f_{ar}^{B}	0.2273
M_{o}^{C}	0.6603	f_{ar}^{SP}	0.2843
T_{dd}^{G}	17.79	X_{b}	0.3759
T_{dd}^{L}	124.6	X_{b}'	0.3375
		X_{b}''	0.4298

Elemental Analysis

%C	89.06
%H	8.36
MW	12.01
$(H/C)_T$	1.1274

Structural Parameters

C_{ar}	18.46
C_{al}	11.95
sigma+1	5.25
P_{o}	0.1440
BL	0.7554
SC	4.4923
MW_{c}	411.68
M_{δ}	35.0498

Comments: 8/11/95   Sample: HRI POC-1, O-43

Dir: CONSOL
fn^{dd}:   con14.1ddft   Contact: S. Brandes
fn^{cp}:   con14.1cp
ct: 2 msec
temp: 23°C

Data pts. at 140, 160, 180 and 200 μsec were excluded from the analysis.

Sample: CONSOL 15

<u>Integration of ^{13}C CP Spectrum</u>

A_{0-90}	91.0000
A_{90-240}	117.2000
$A_{165-240}$	1.5000
$A_{150-165}$	3.9000
A_{90-165}	116.0000
$A_{135-150}$	27.8000
A_{0-25}	28.1000
A_{50-60}	4.3000
A_{50-90}	5.3000

<u>^{13}C Spectrum Dipolar Dephasing</u>

M_o^{CH}	0.4898
M_o^{C}	0.5094
T_{dd}^{G}	22.06
T_{dd}^{L}	224.9

<u>Elemental Analysis</u>

%C	91.76
%H	5.83
MW	12.01
$(H/C)_T$	0.7631

f_{ar}	0.5629
f_{al}	0.4371
f_{ar}'	0.5557
f_{CO}	0.0072
f_{ar}^{P}	0.0187
f_{ar}^{S}	0.1332
$f_{al}^{CH3OCH3}$	0.1556
f_{al}^{CHCH2}	0.2815
f_{al}^{CO}	0.0091
f_{ar}^{CH}	0.4902
f_{ar}^{C}	0.5098
$f_{ar}^{CH'}$	0.2724
$f_{ar}^{C'}$	0.2833
f_{ar}^{B}	0.1314
f_{ar}^{SP}	0.2733
X_b	0.2365
X_b'	0.2347
X_b''	0.2716

<u>Structural Parameters</u>

C_{ar}	11.31
C_{al}	8.89
sigma+1	3.09
P_o	-0.0247
BL	-0.0764
SC	3.1668
MW_c	266.35
M_δ	40.4802
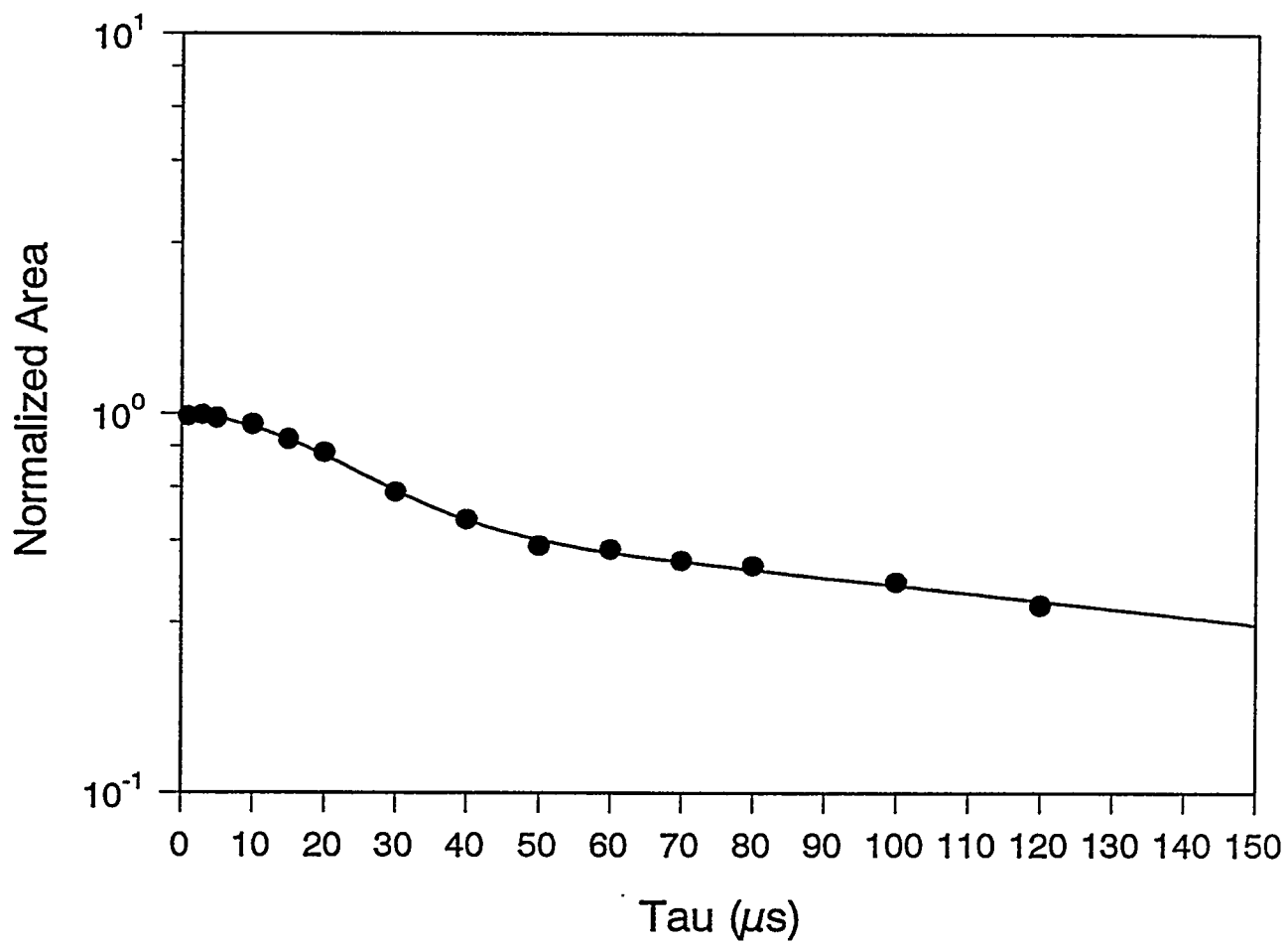
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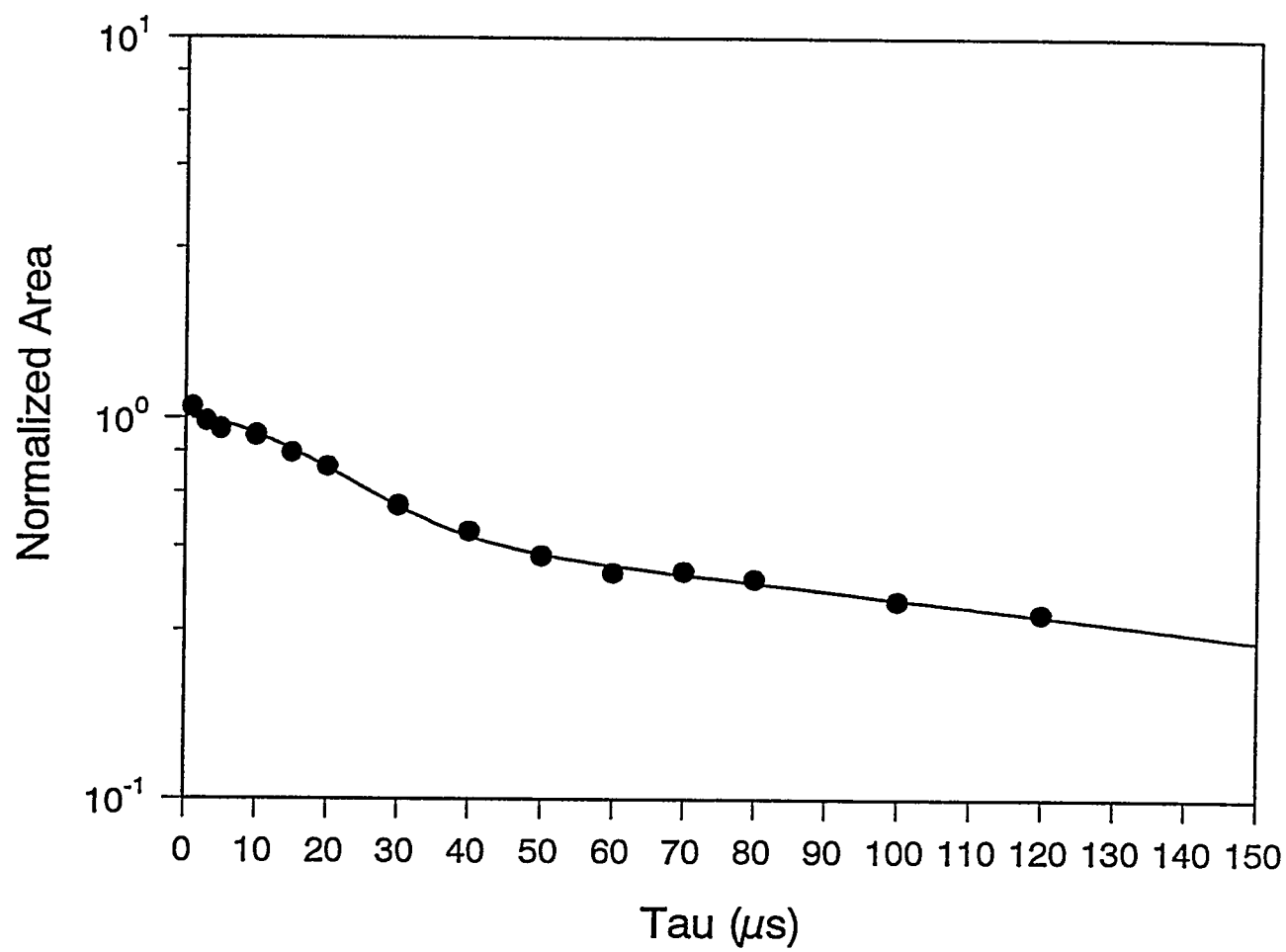
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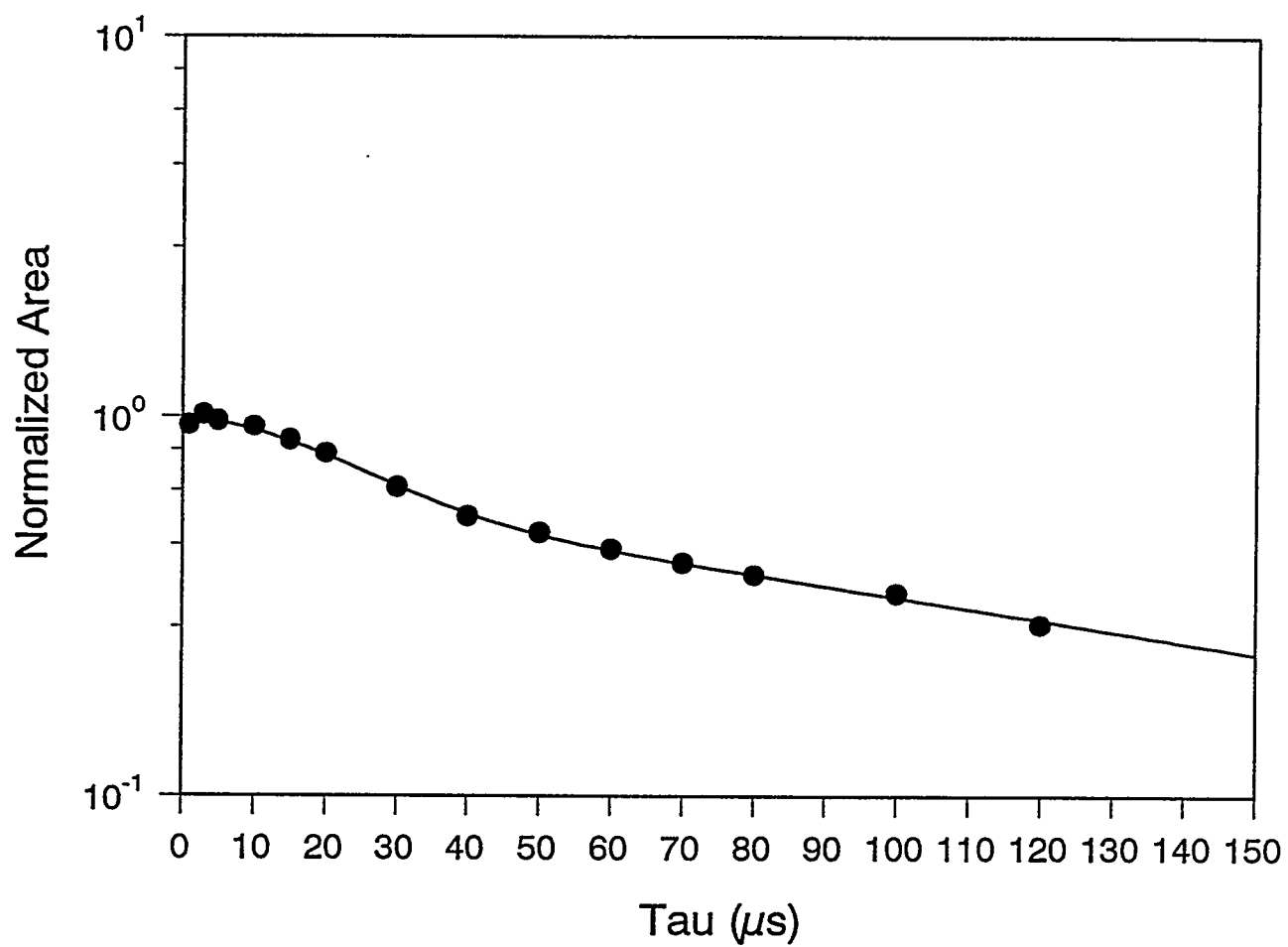
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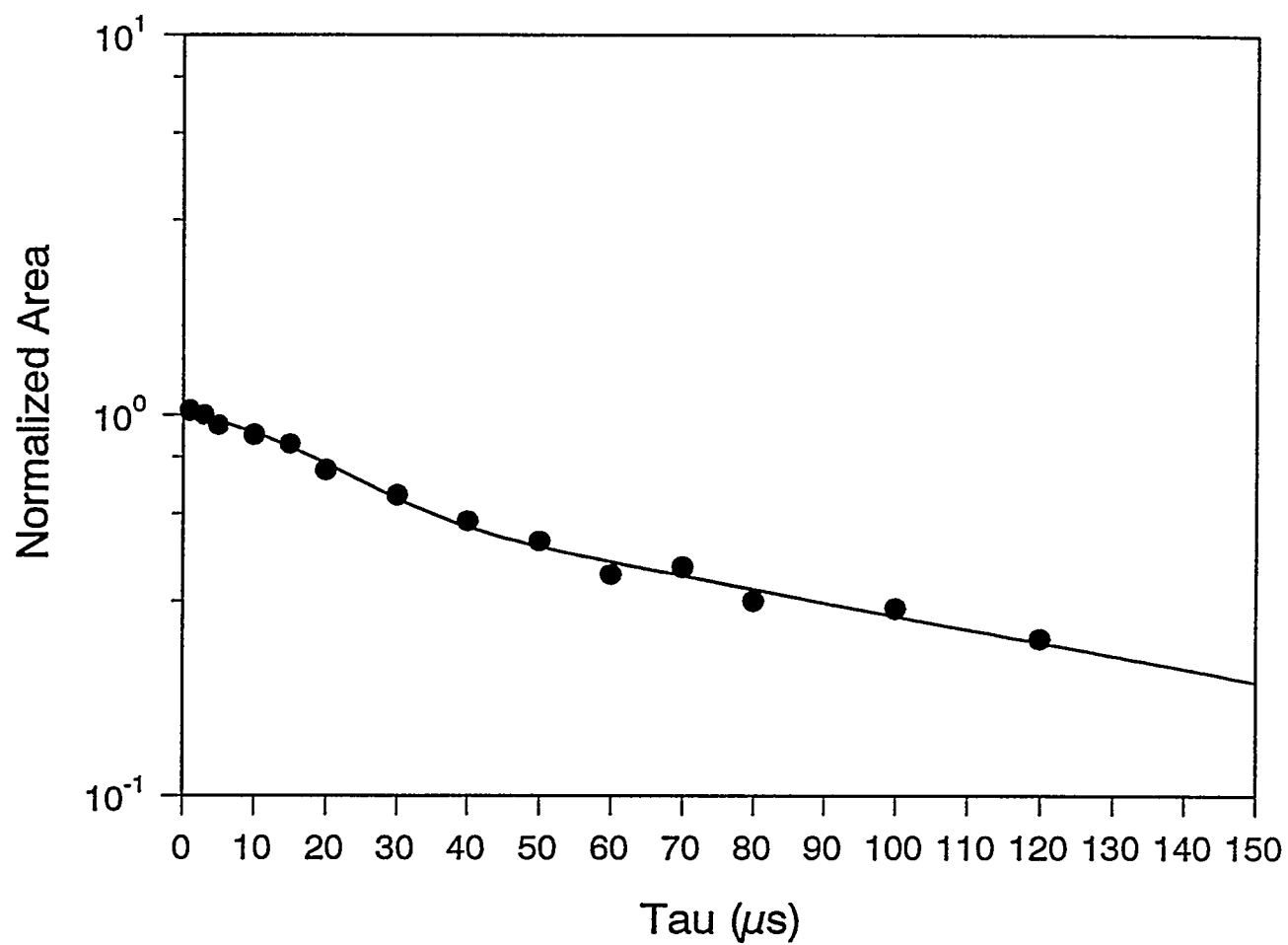
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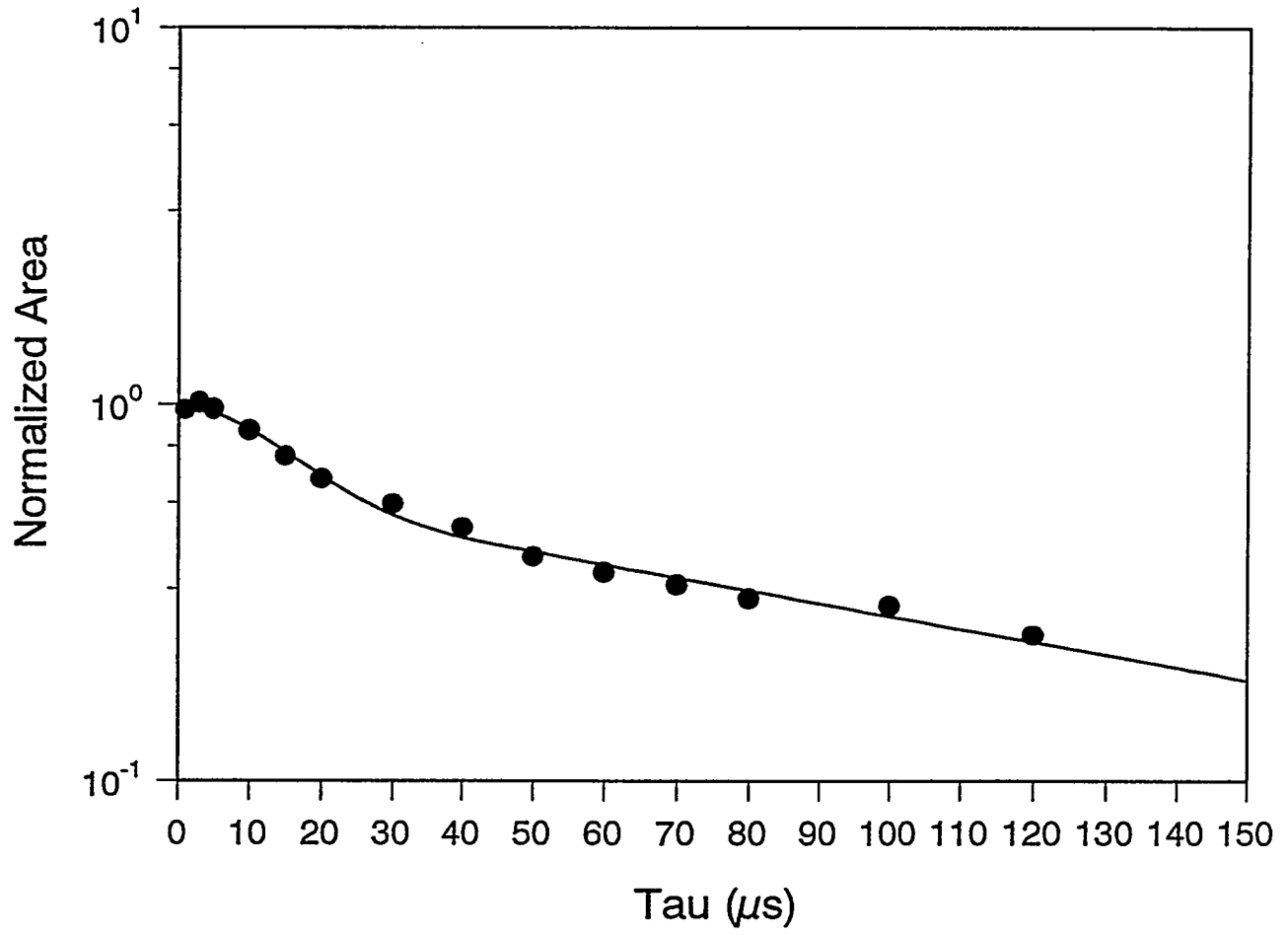
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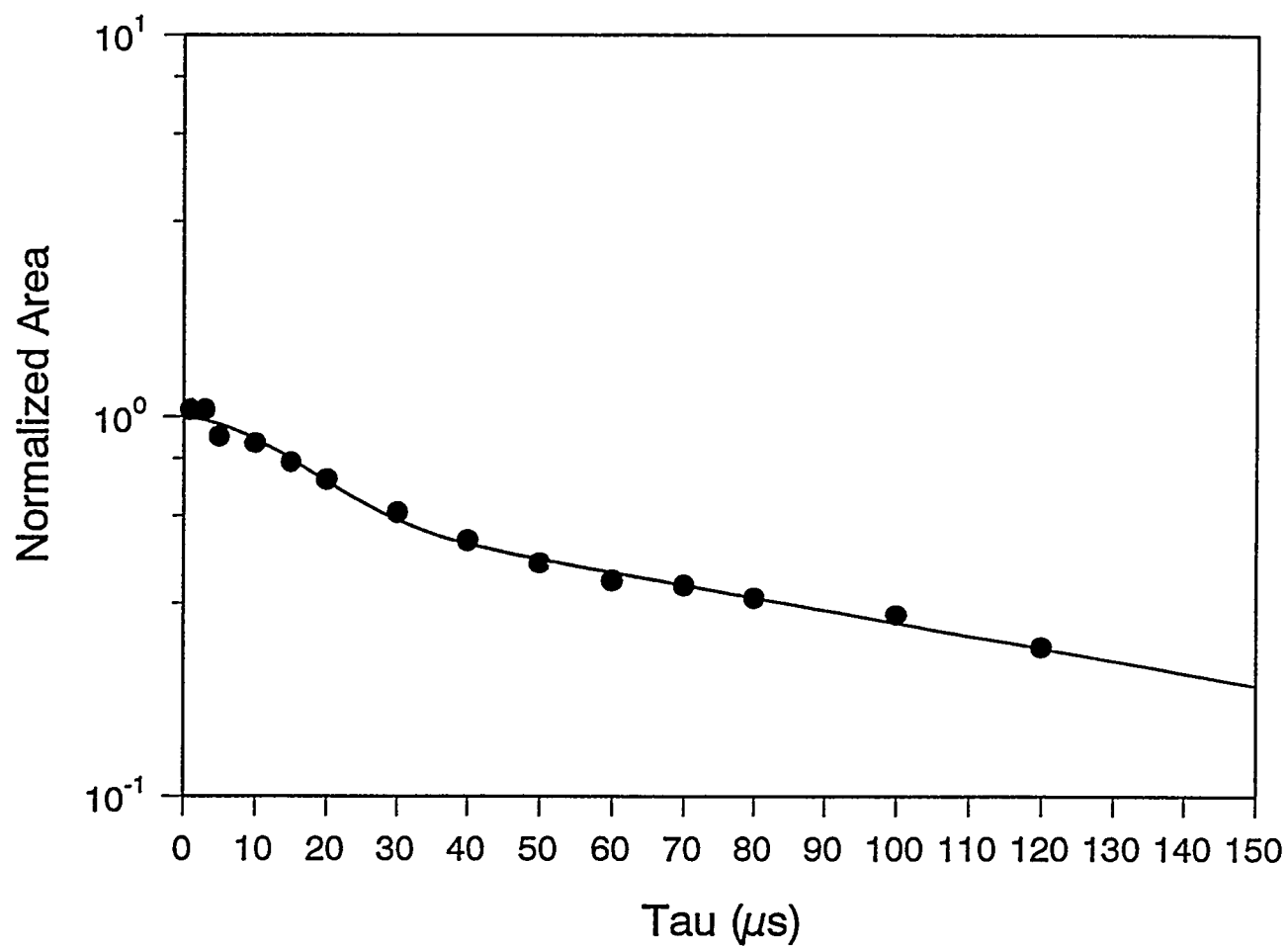
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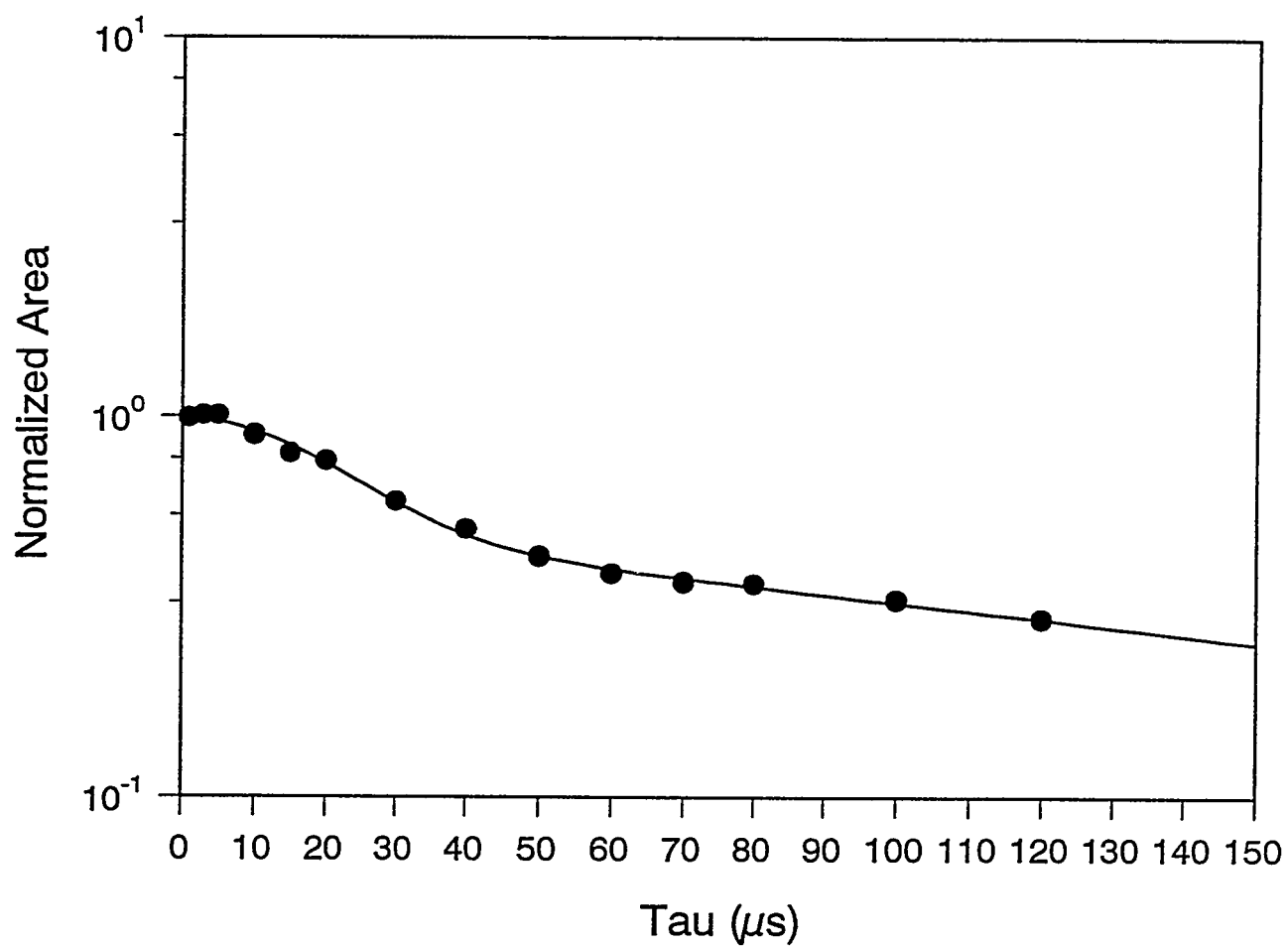
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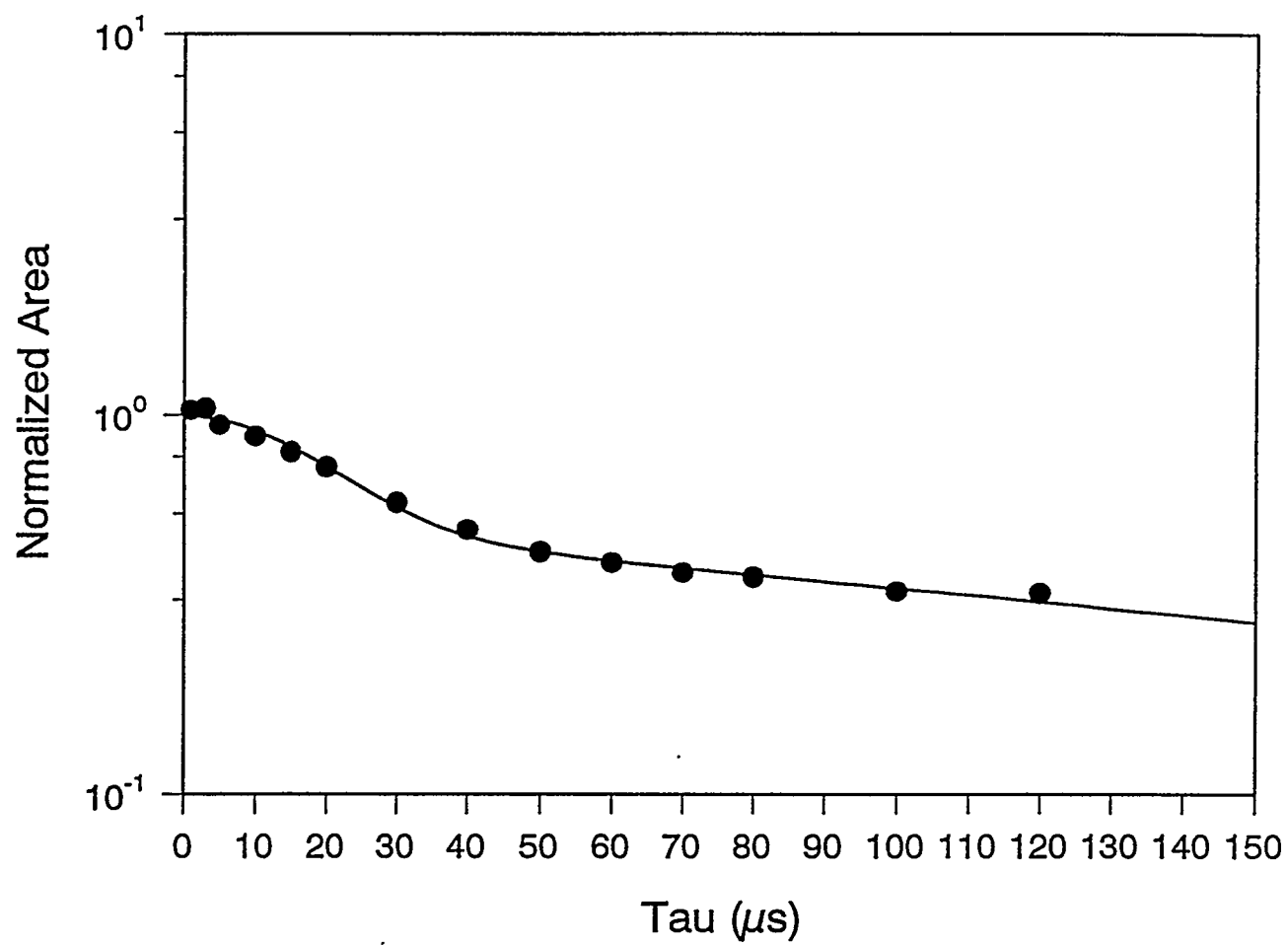
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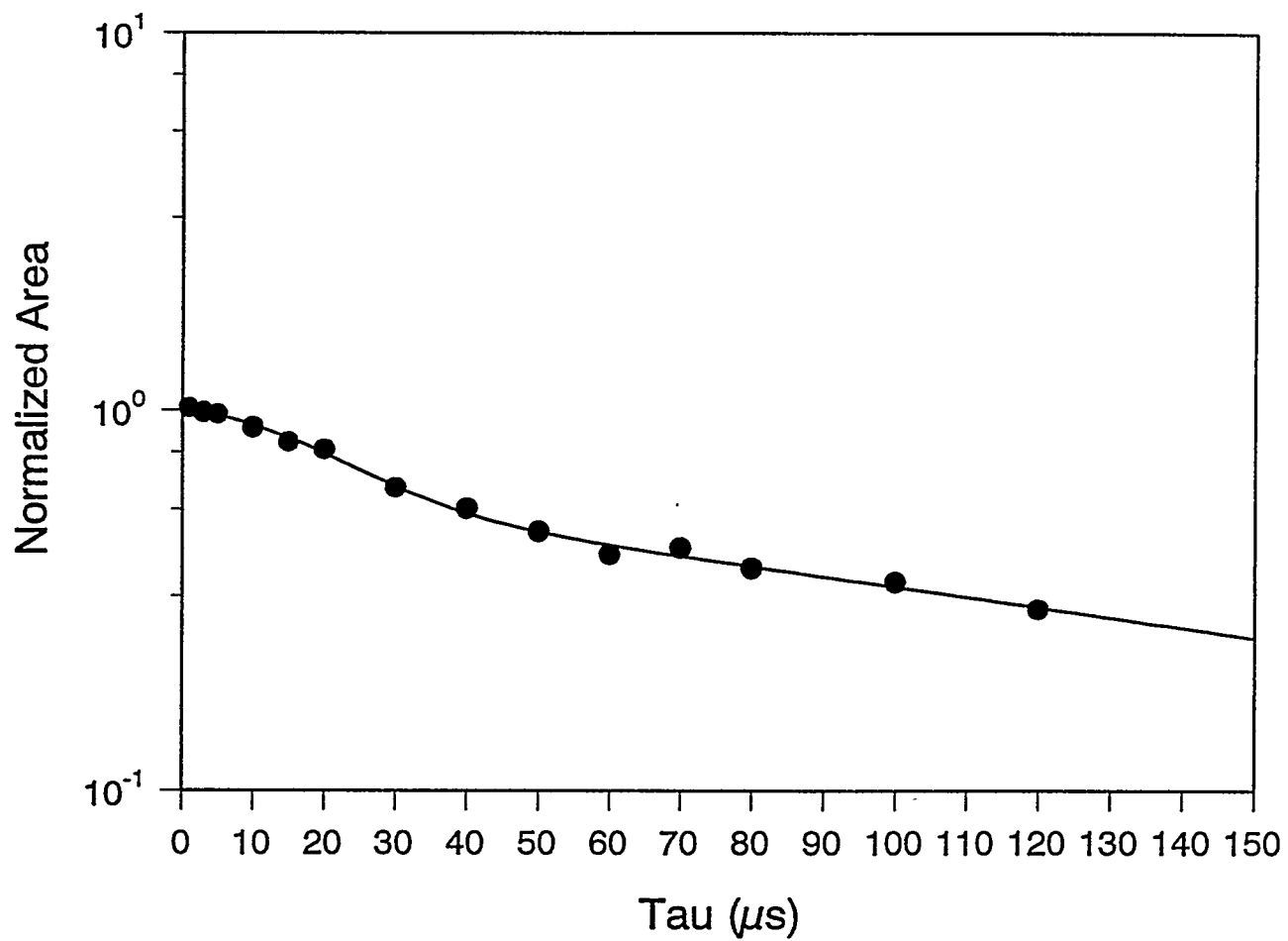
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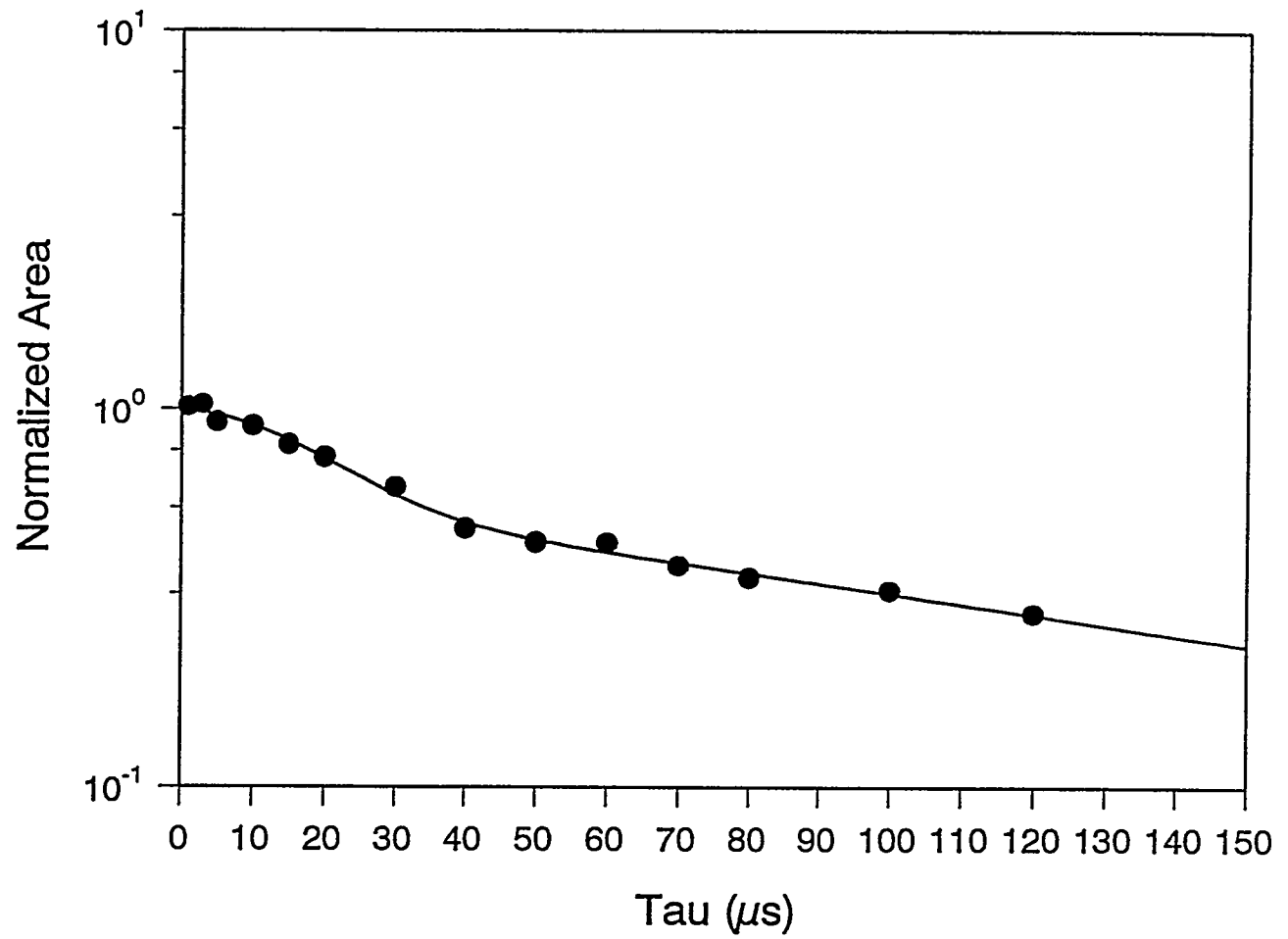
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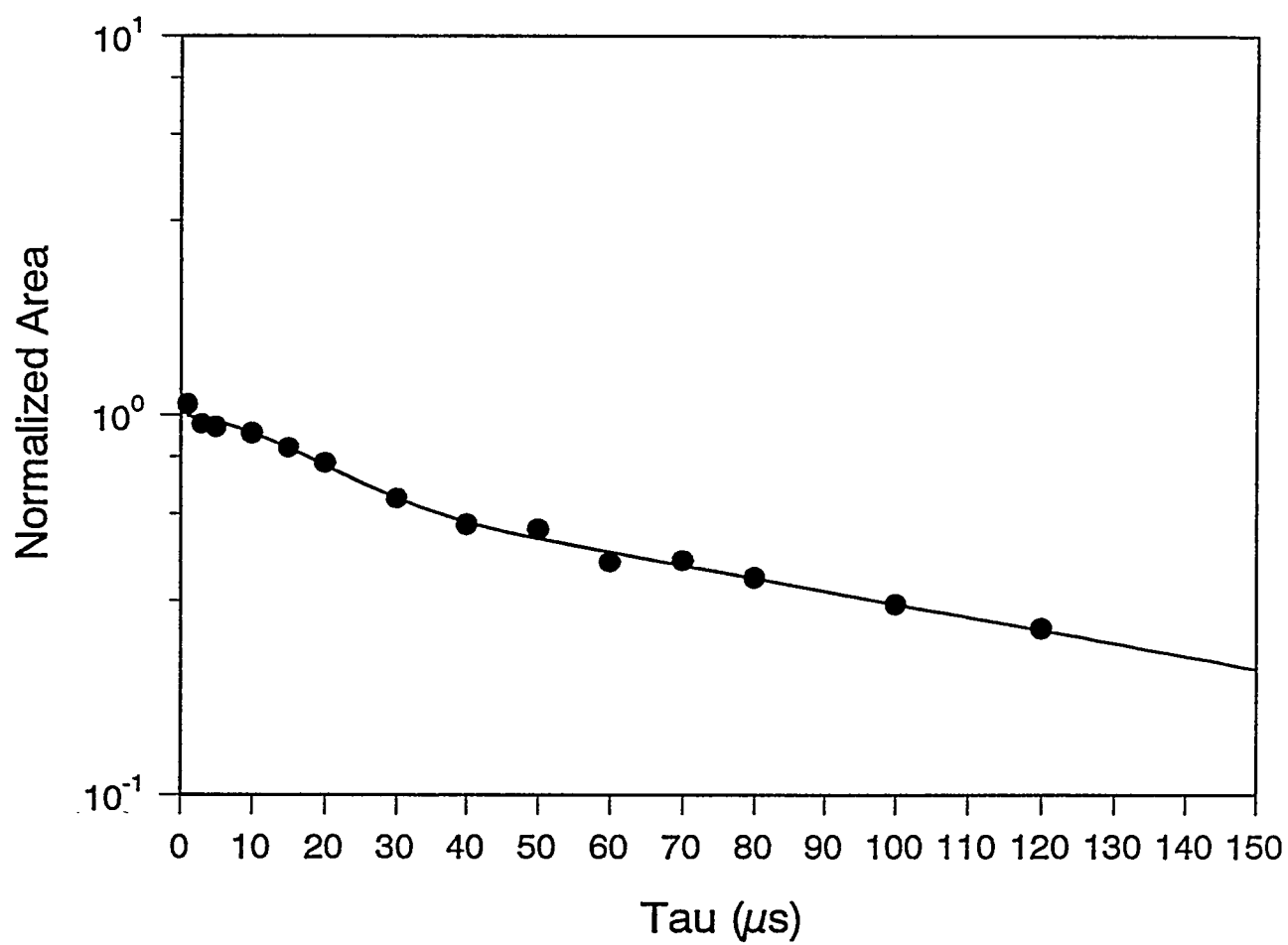
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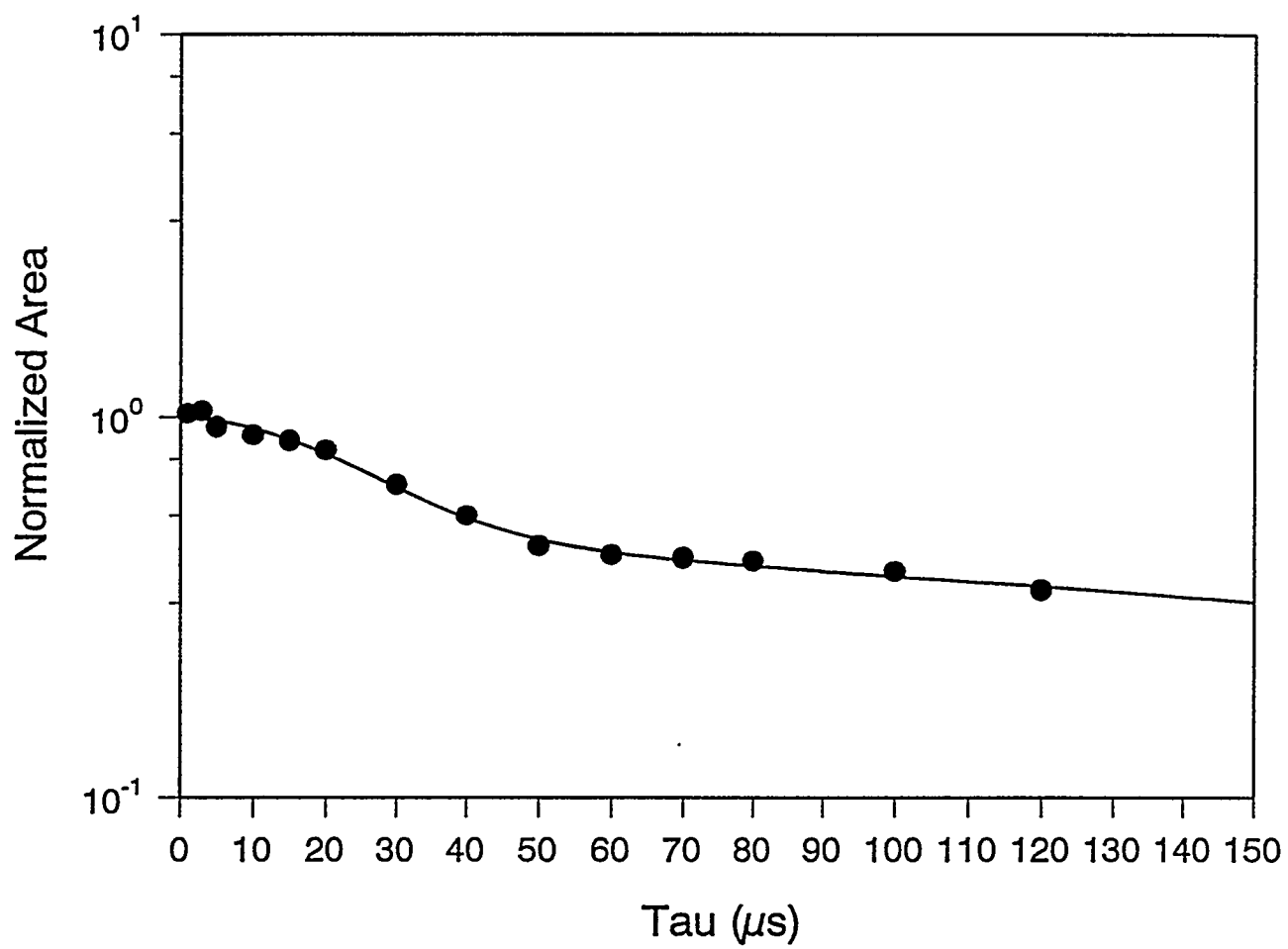
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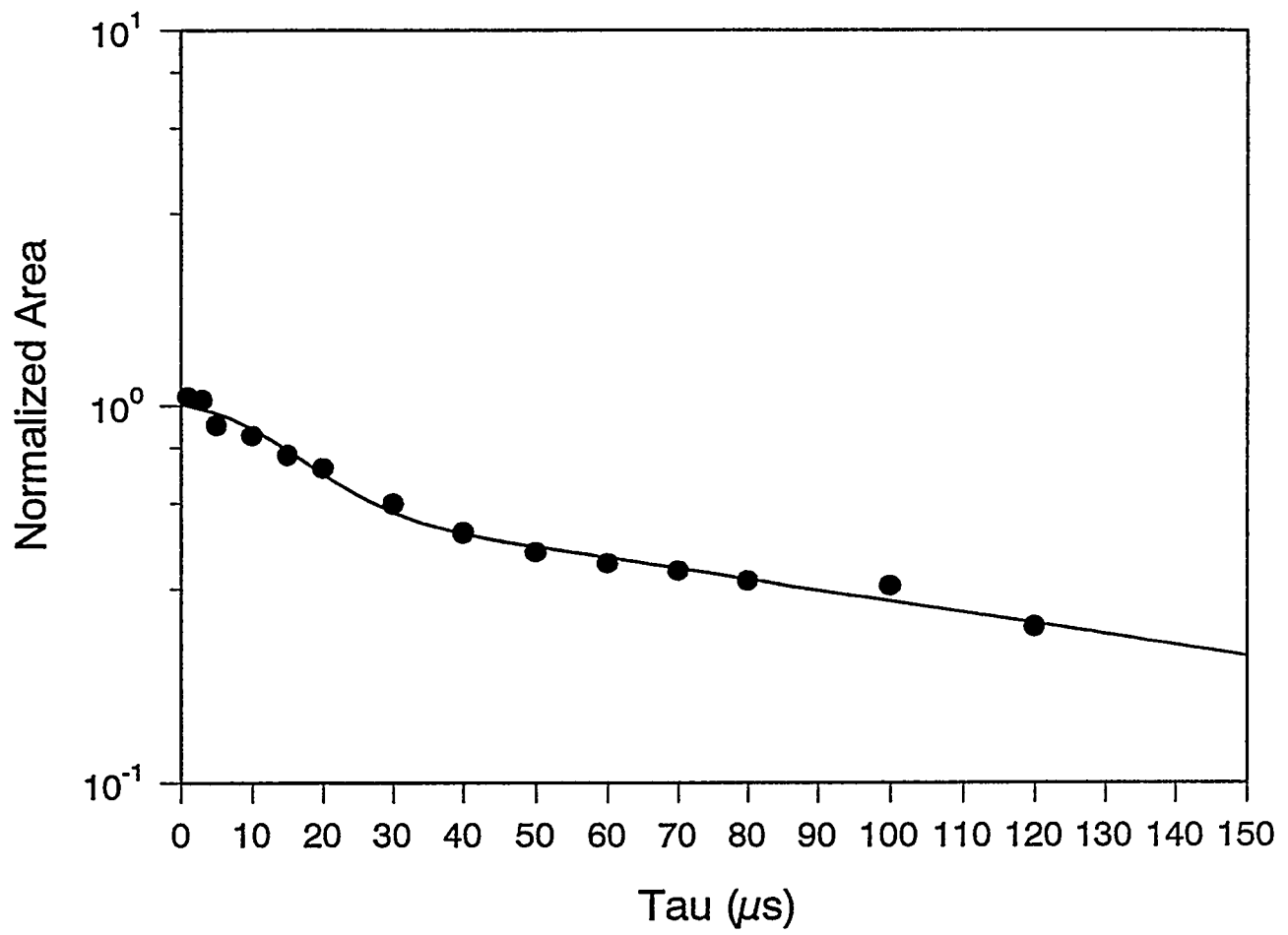
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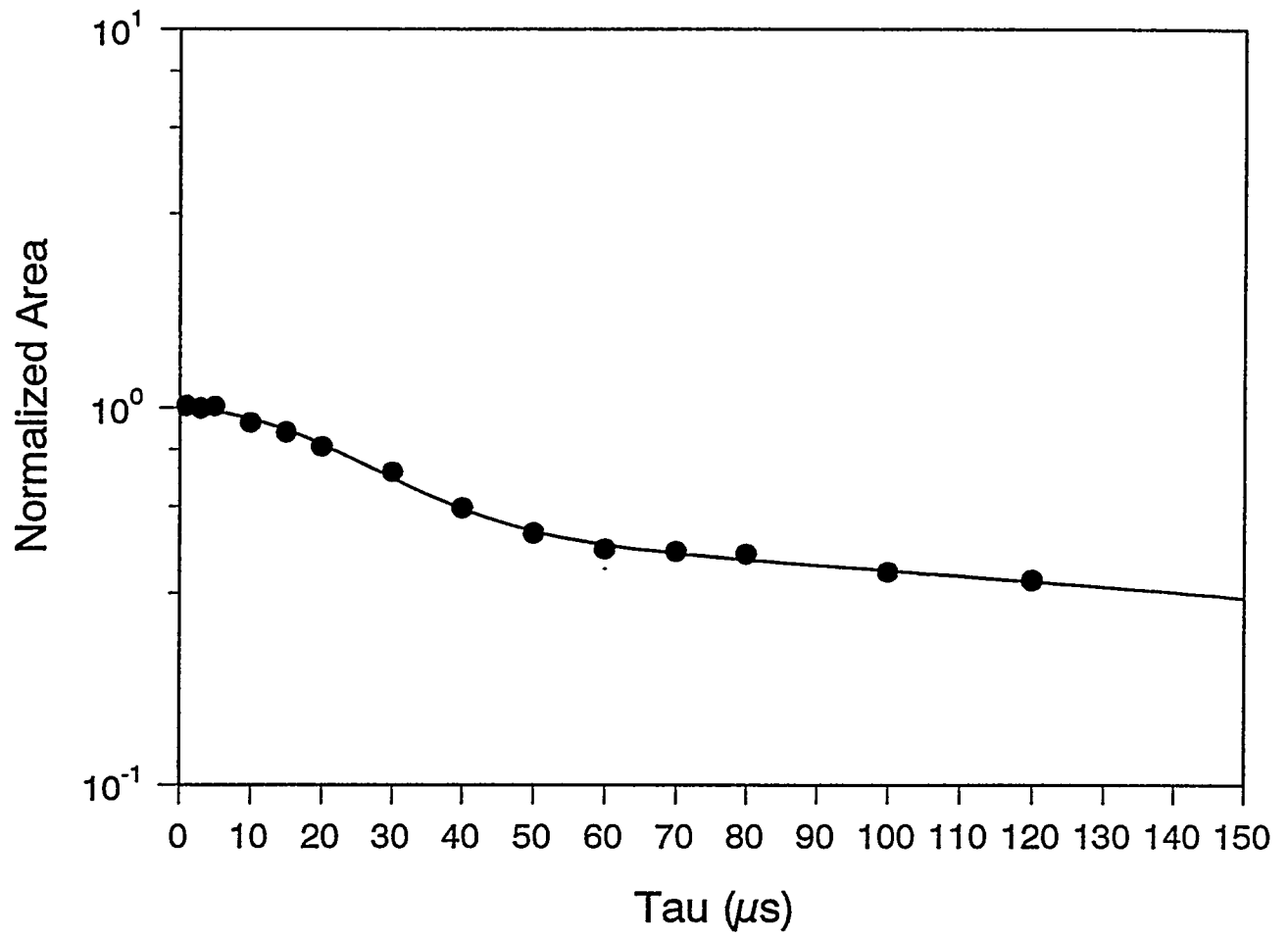
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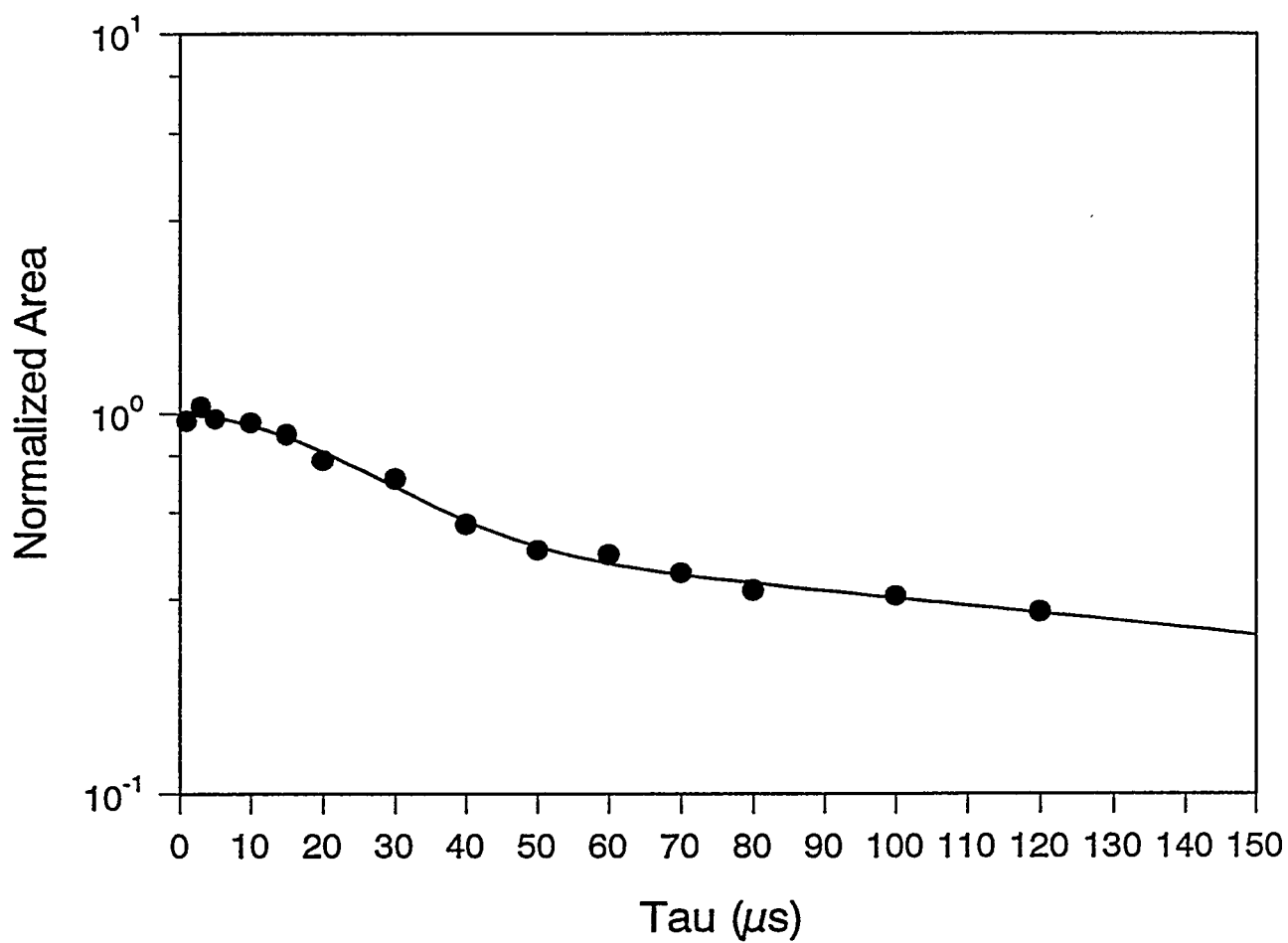
Structural Parameter Calculations for Sample 2

$$\left(\frac{H}{C}\right)_T = \frac{\%H \times 12}{\%C} = \frac{6.19 \times 12}{90.12} = .825$$

$$f_{ar} = \frac{A_{90-240}}{A_{90-240} + A_{0-90}} = \frac{167.2}{167.2 + 53.8} = ..7566$$

$$f_{CO} = f_{ar} \times \frac{A_{165-240}}{A_{90-240}} = .7566 \times \frac{1.40}{167.2} = .0063$$

$$f_{ar}{}' = f_{ar} - f_{CO} = .7566 - .0063 = .7502$$

$$f_{ar}{}^P = f_{ar}{}' \times \frac{A_{150-165}}{A_{90-165}} = .7502 \times \frac{7.50}{165.9} = 0.0339$$

$$f_{ar}{}^S = f_{ar}{}' \times \frac{A_{135-150}}{A_{90-165}} = .7502 \times \frac{38.0}{165.9} = .1718$$

$$f_{al} = 1 - f_{ar} = 1 - .7566 = .2434$$

$$f_{al}{}^{CH3OCH3} = f_{al} \times \frac{A_{0-25} + A_{50-60}}{A_{0-90}} = .2434 \times \frac{22.1 + 1.5}{53.8} = .1068$$

$$f_{al}{}^{CHCH2} = f_{al} - f_{al}{}^{CH3OCH3} = .2434 - .1068 = .1367$$

$$f_{al}{}^{CO} = f_{al}{}^{CH3OCH3} \times \frac{A_{50-90}}{A_{0-90}} = .1068 \times \frac{1.5}{53.8} = .0030$$

$$f_{ar}{}^{CH} = \frac{M_o{}^{CH}}{M_o{}^{CH} + M_o{}^C} = \frac{.4486}{.4486 + .5514} = .4486$$

$$f_{ar}{}^C = \frac{M_o{}^C}{M_o{}^{CH} + M_o{}^C} = \frac{.5514}{.4486 + ..5514} = .5514$$

$$f_{ar}{}^{CH'} = f_{ar}{}' \times f_{ar}{}^{CH} = .7502 \times .4486 = .3365$$

$$f_{ar}{}^{C'} = f_{ar}{}' \times f_{ar}{}^C = .7502 \times .5514 = .4577$$

$$f_{ar}{}^B = f_{ar}{}^{C'} - f_{ar}{}^P - f_{ar}{}^S = .5514 - .0339 - .1718 = .2079$$

$$f_{ar}{}^{SP} = \frac{f_{ar}{}^S + f_{ar}{}^P}{f_{ar}{}'} = \frac{.1718 + .0339}{.7502} = .2743$$

Lattice Parameter Calculations for Sample 2

$$X_b = \frac{f_{ar}{}^B}{f_{ar}{}'} = \frac{.2079}{.7502} = .2772$$

$$X_b = \frac{1}{2} \times \left[1 - \tanh\left(\frac{C_{ar} - C_o}{m}\right)\right] \times X_b{}' + \frac{1}{2} \times \left[1 + \tanh\left(\frac{C_{ar} - C_o}{m}\right)\right] \times X_b{}''$$

$$.2772 \quad = \frac{1}{2} \times \left[1 - \tanh\left(\frac{C_{ar} - 19.01}{4.15}\right)\right] \times .2742 + \frac{1}{2} \times \left[1 + \tanh\left(\frac{C_{ar} - 19.01}{4.15}\right)\right] \times .3280$$

Iterating with the above equation and the next two equations : $C_{ar} = 13.287$

$$X_b{}' = \frac{1}{2} - \frac{3}{C_{ar}} = \frac{1}{2} - \frac{3}{13.287} = .2742$$

$$X_b{}'' = 1 - \sqrt{\frac{6}{C_{ar}}} = 1 - \sqrt{\frac{6}{13.287}} = .3280$$

$$C_{al} = \frac{\%C \times MW_c}{1200 \times f_{al}} = \frac{13.287 \times 236.03}{1200 \times .2434} = 4.3151$$

$$\sigma + 1 = \left(f_{ar}{}^S + f_{ar}{}^P\right) \times \frac{C_{ar}}{f_{ar}{}'} = (.1718 + .0339) \times \frac{13.287}{.7502} = 3.644$$

$$P_o = \frac{f_{ar}{}^P + f_{ar}{}^S - f_{al}{}^{CH3OCH3}}{f_{ar}{}^P + f_{ar}{}^S} = \frac{.0339 + .1718 - .1068}{.0339 + .1718} = .4810$$

$$BL = (\sigma + 1) \times P_o = 3.644 \times .4810 = 1.753$$

$$SC = (\sigma + 1) - BL = 3.644 - 1.753 = 1.891$$

$$MW_c = \frac{1201 \times C_{ar}}{f_{ar}{}' \times \%C} = \frac{1201 \times 13.287}{.7502 \times 90.12} = 236.03$$

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90

135

150

165

100.0

A_{90-165}

A_{90-240}

$A_{135-150}$

$A_{150-165}$

$A_{165-240}$

240

32.9

A_{6-25}

A_{6-90}

A_{50}

A_{50-90}

ppm

0   50   100   150   200   250

WRI NMR Center
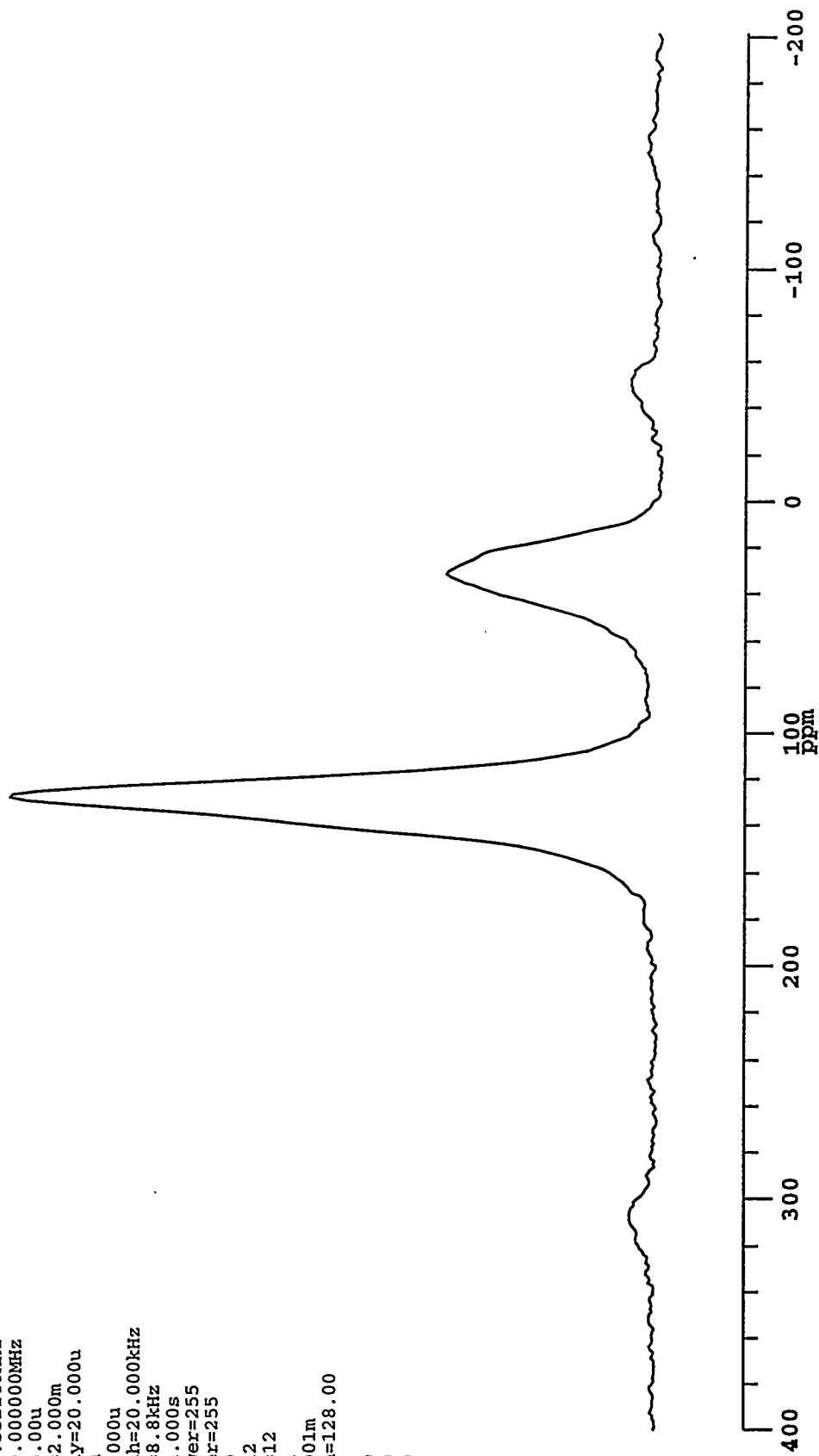
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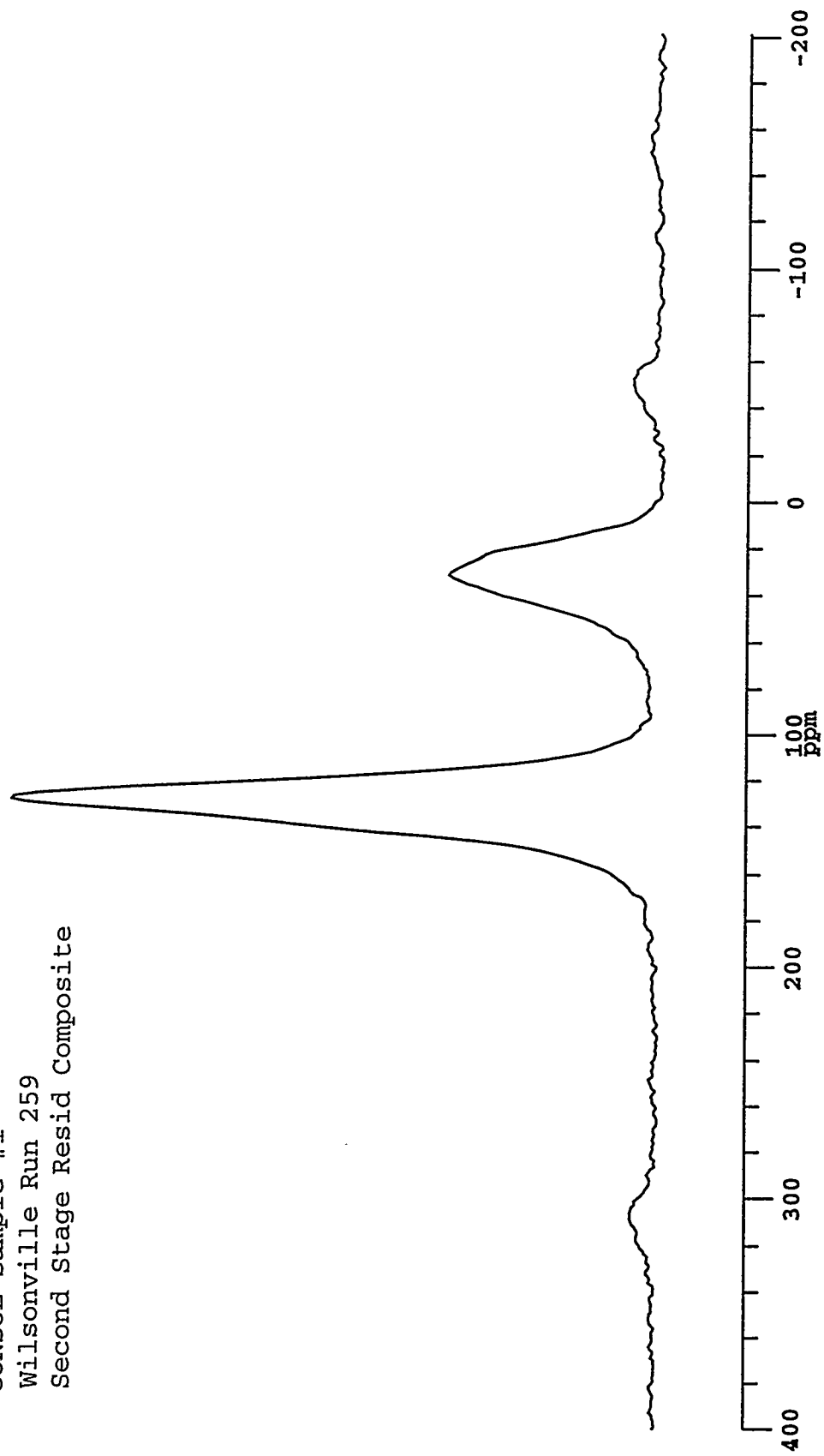
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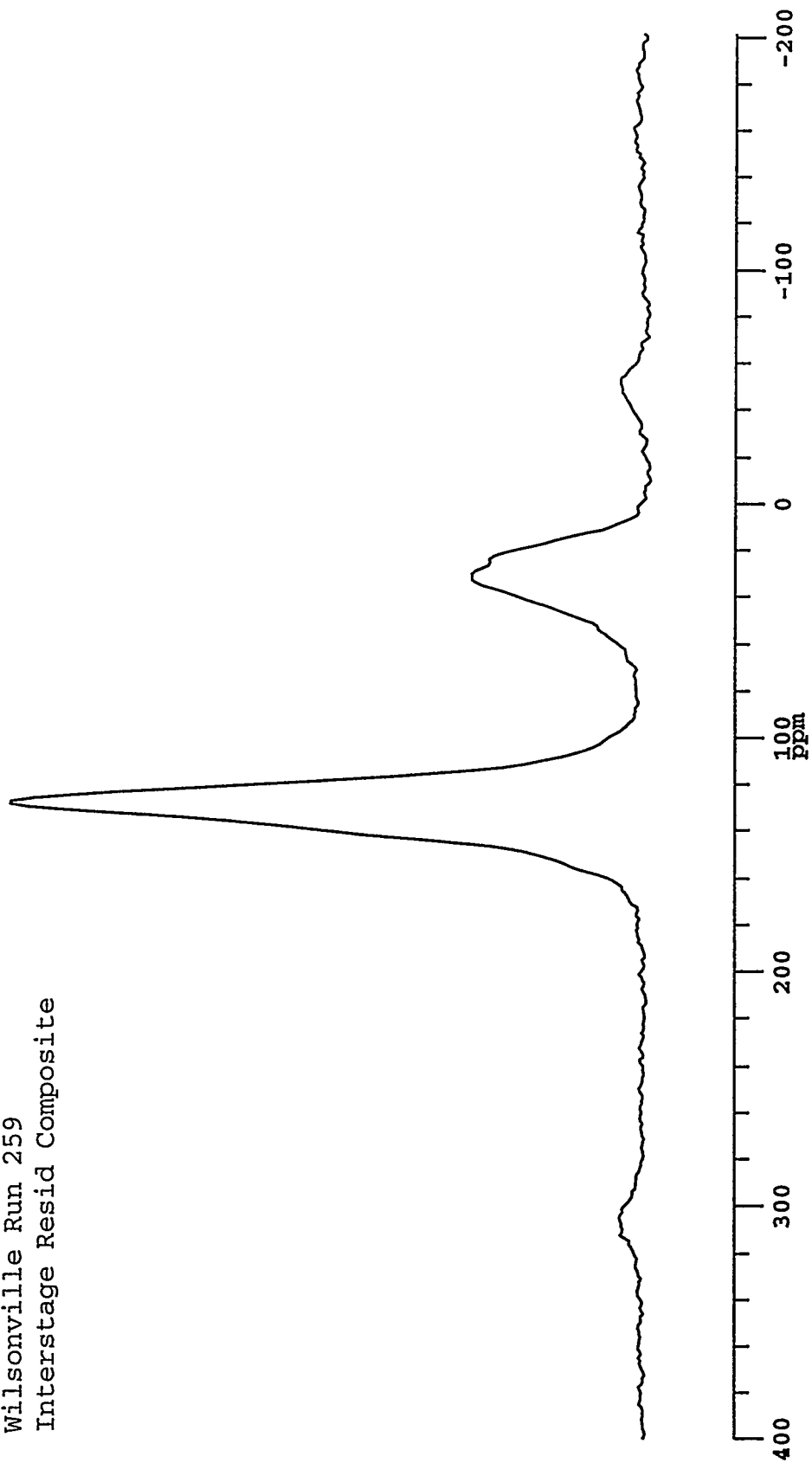
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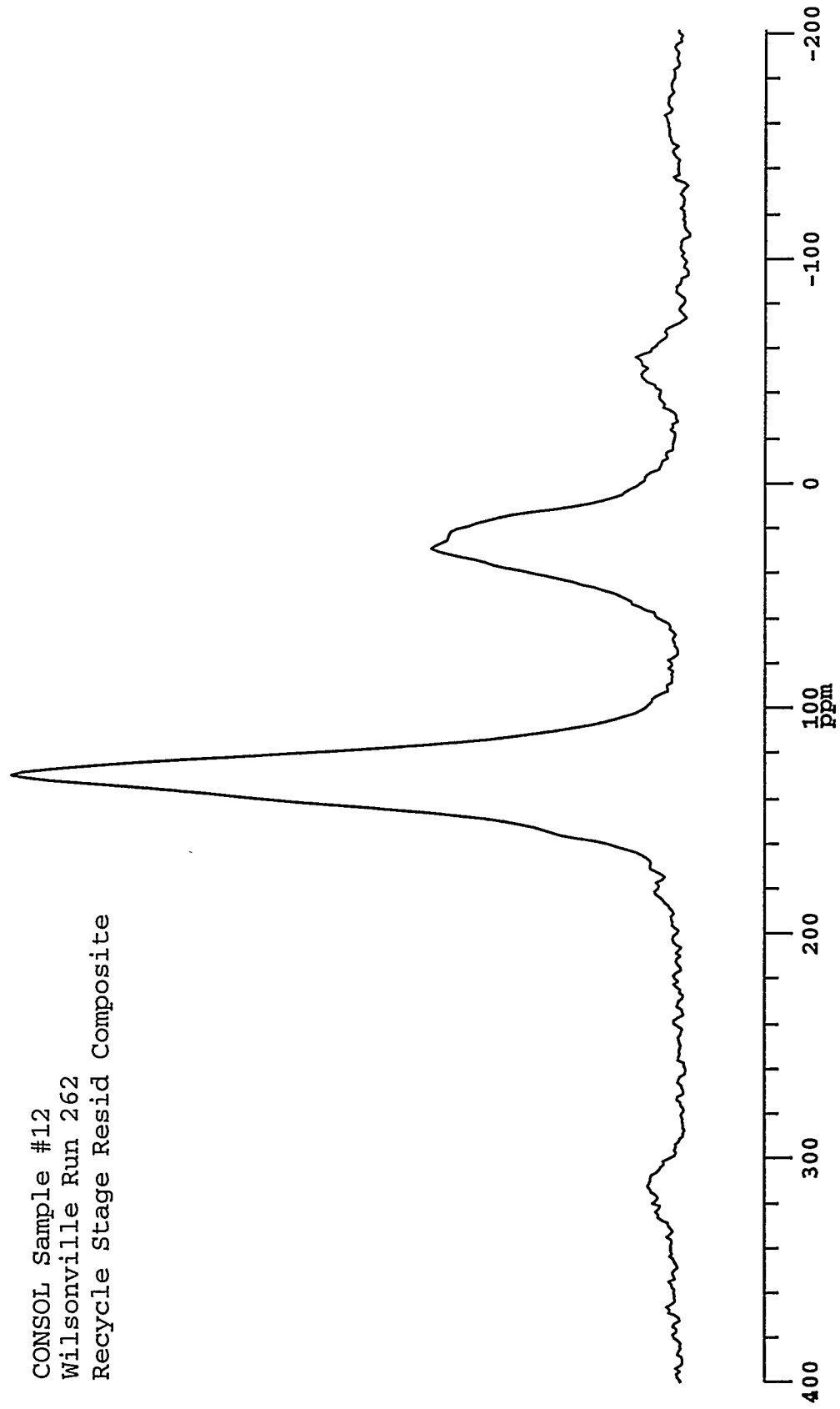Wilsonville Run 259
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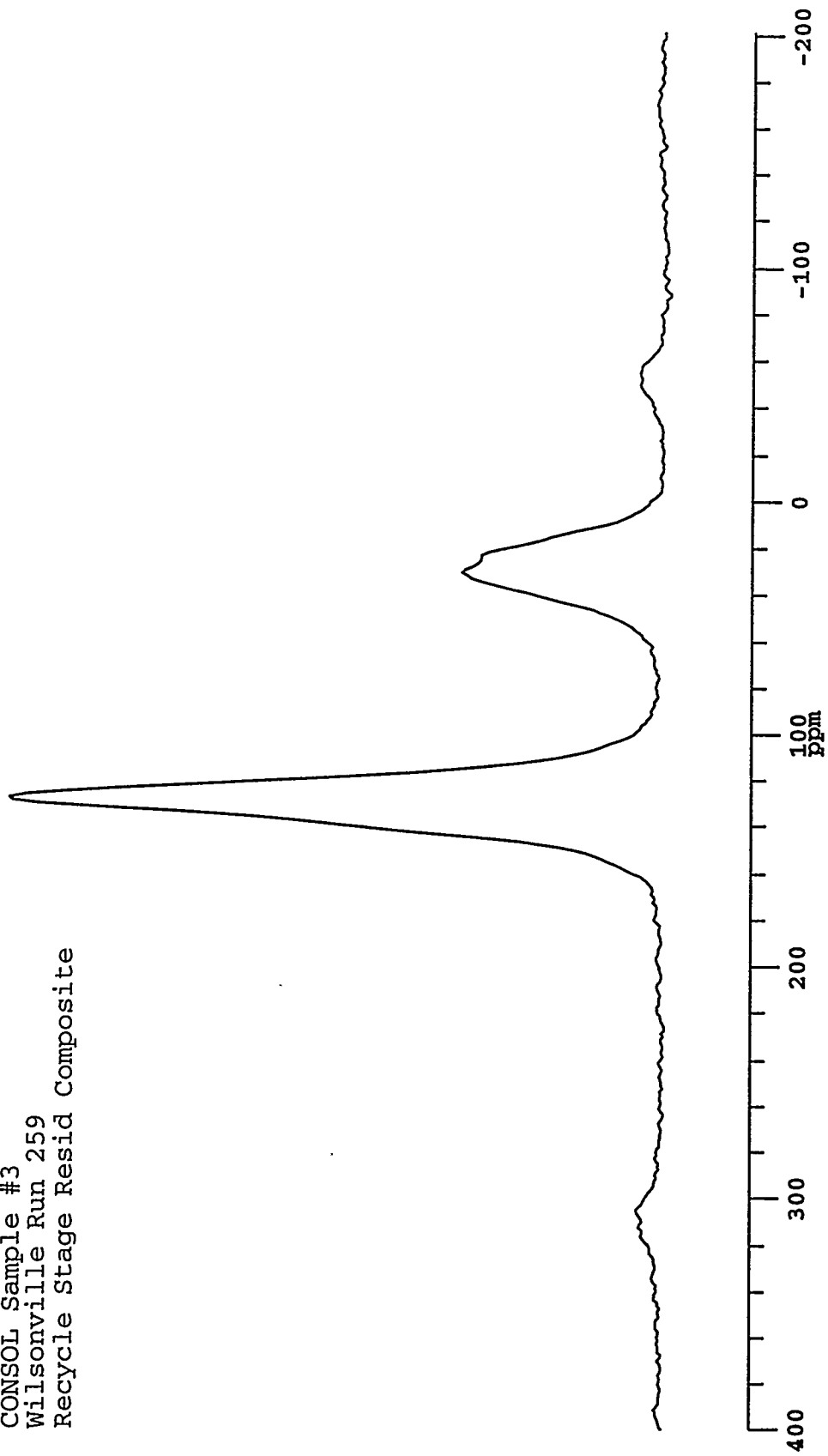
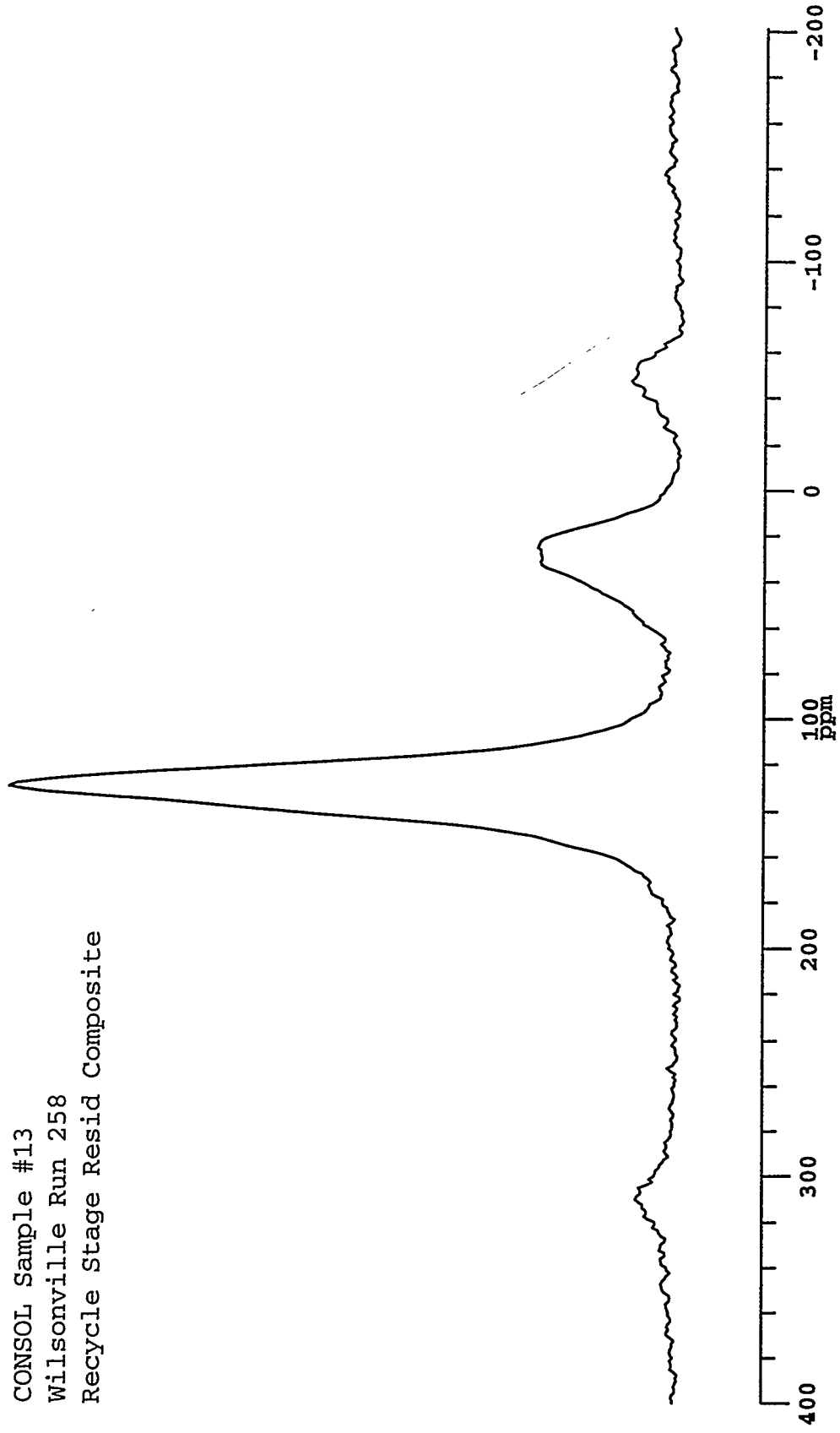CONSOL Sample #4
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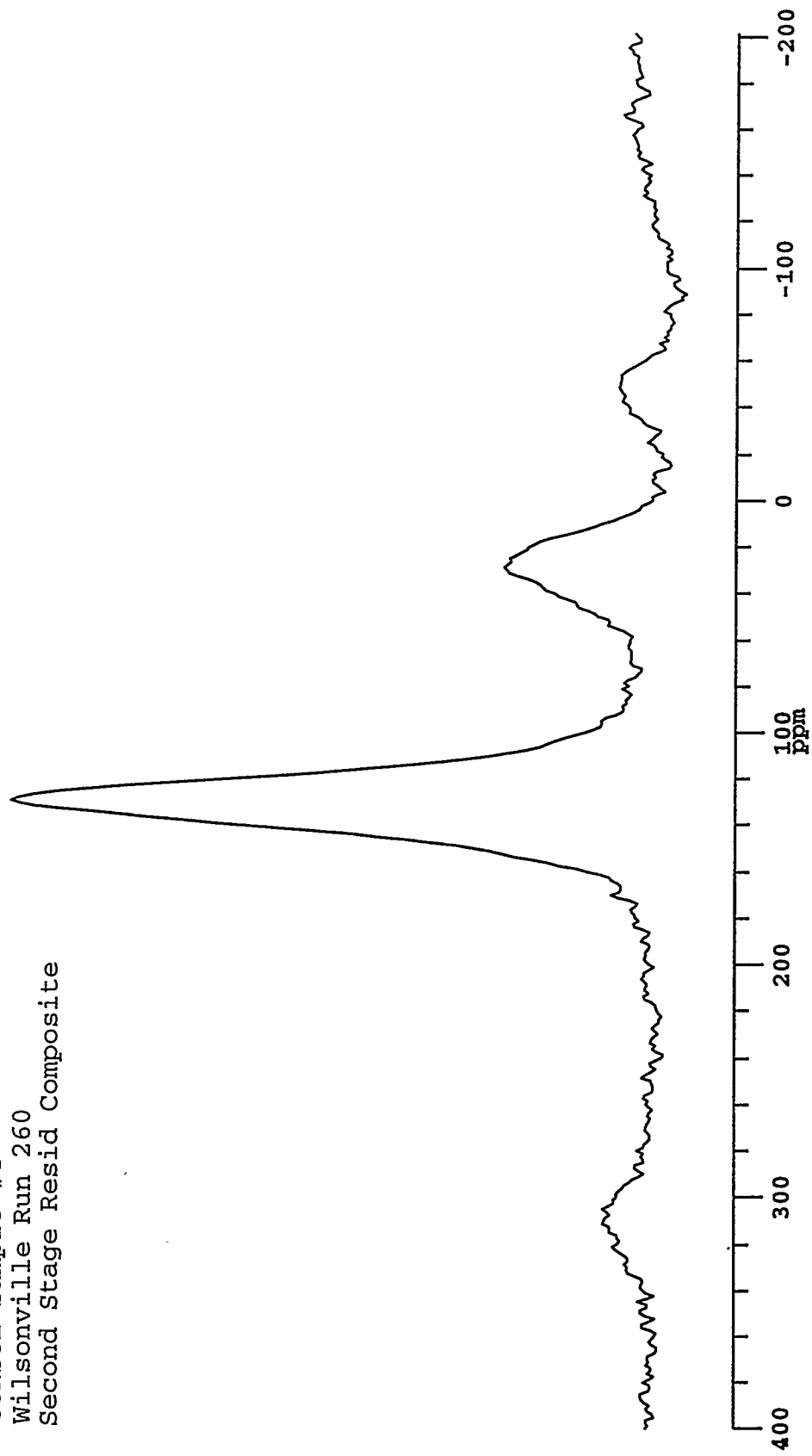
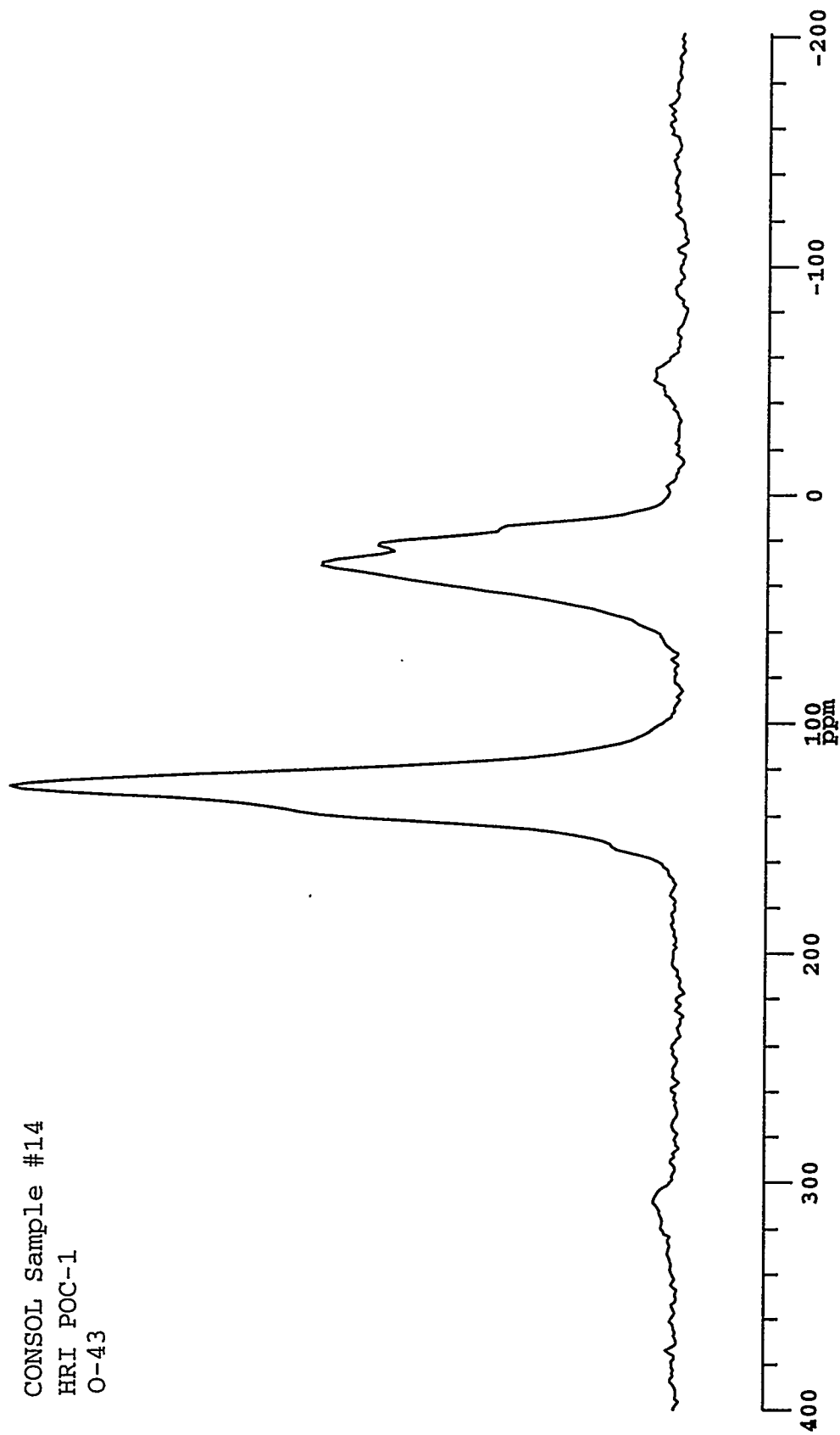CONSOL Sample #5
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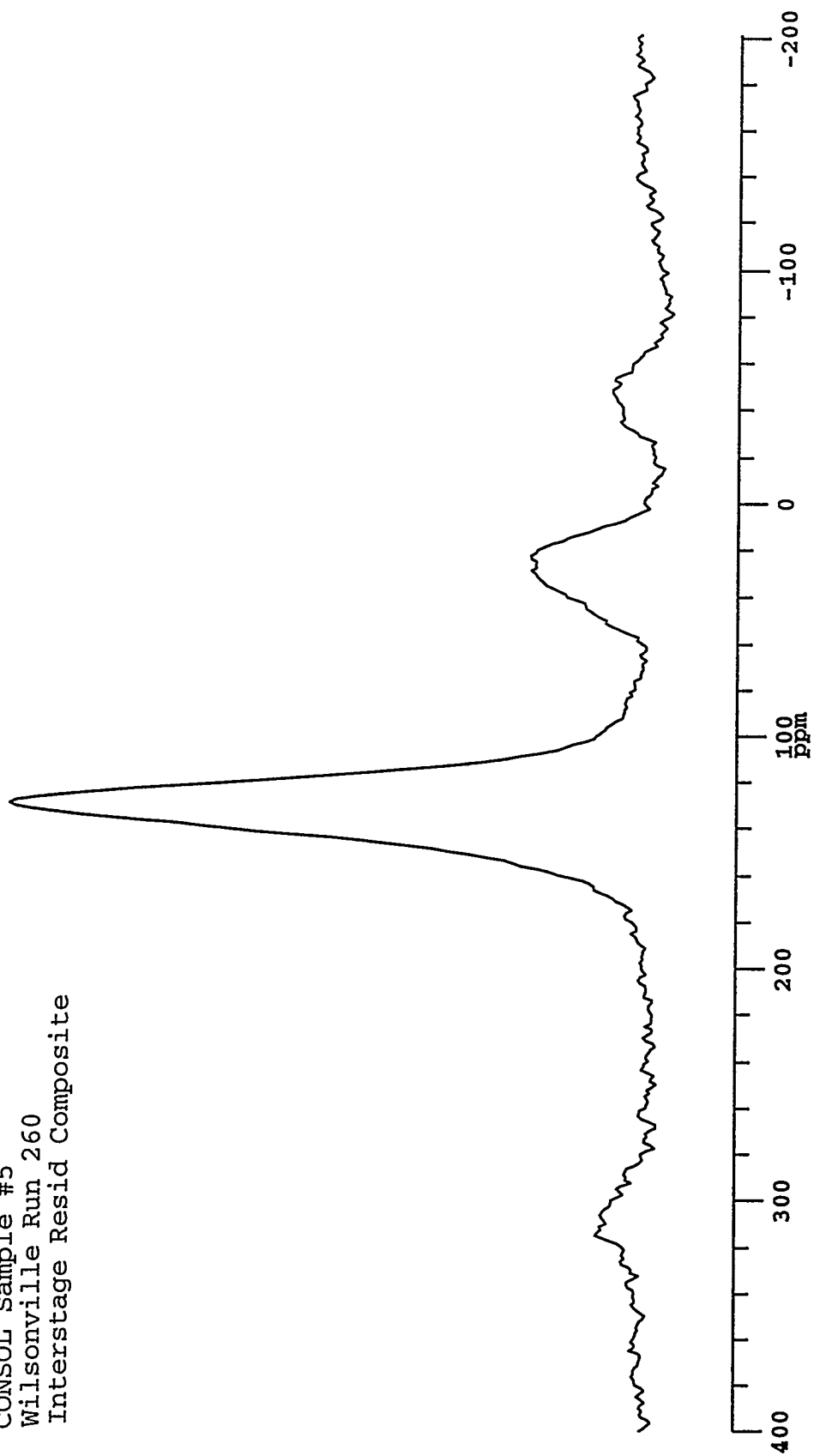
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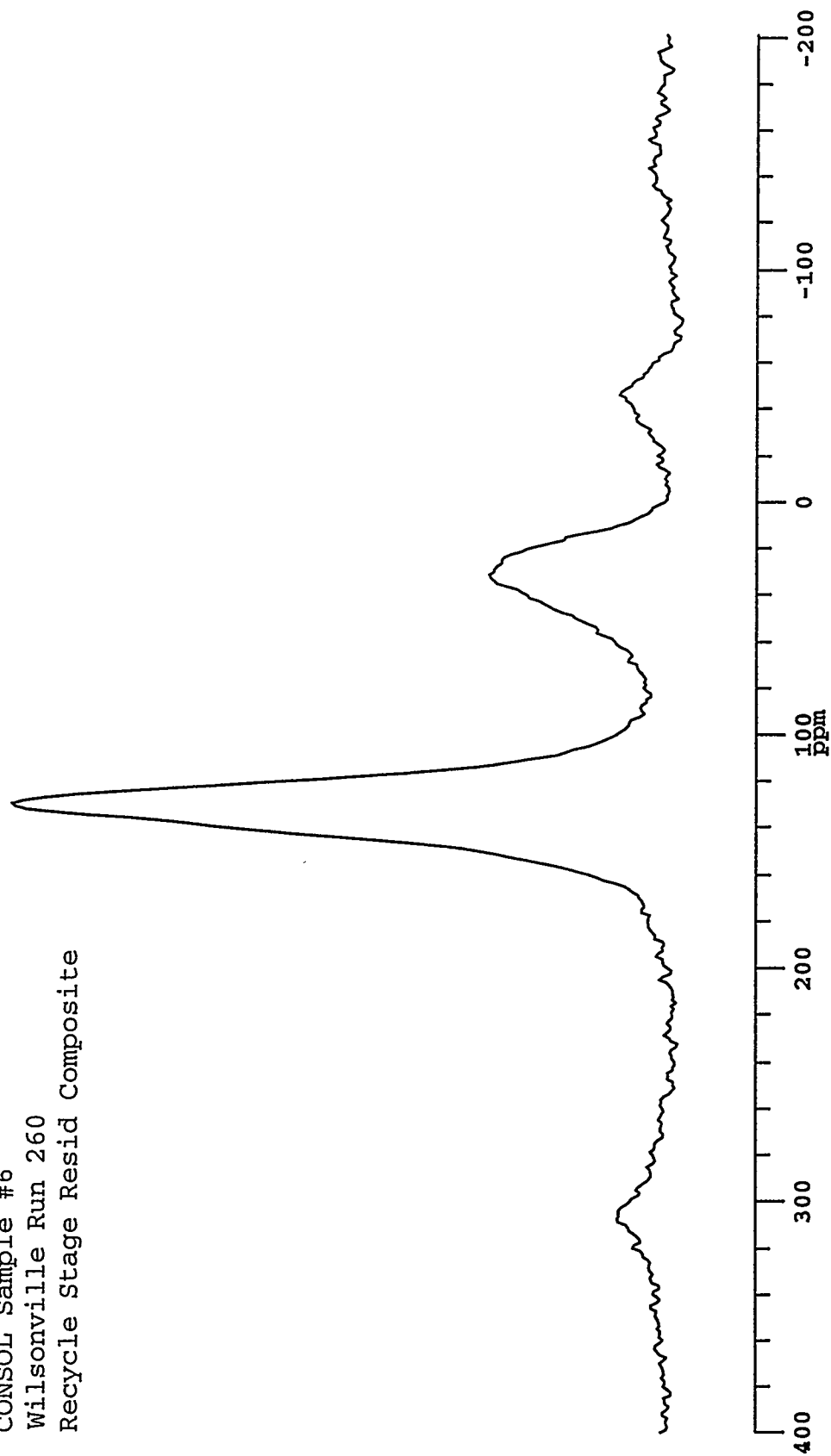
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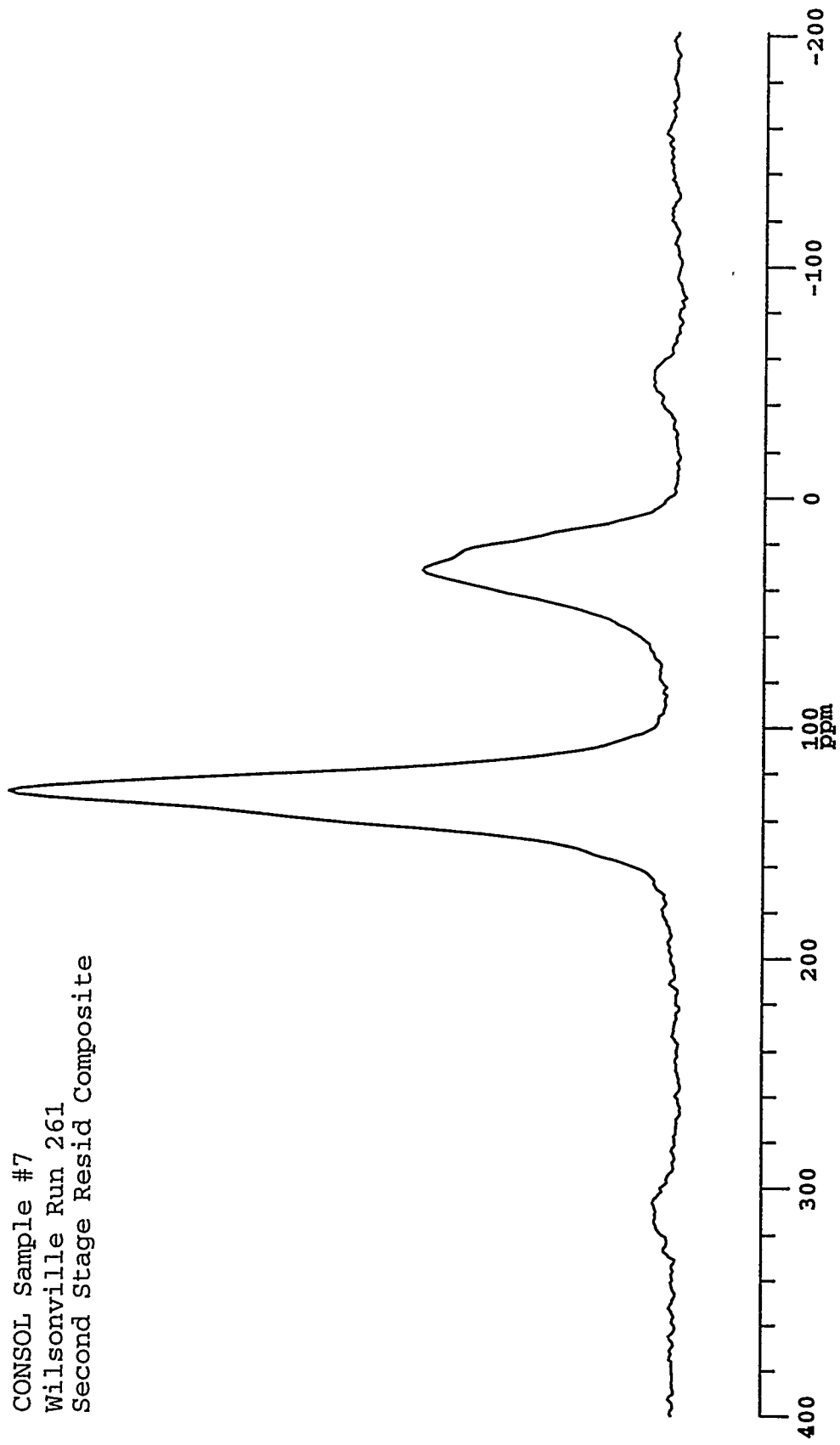
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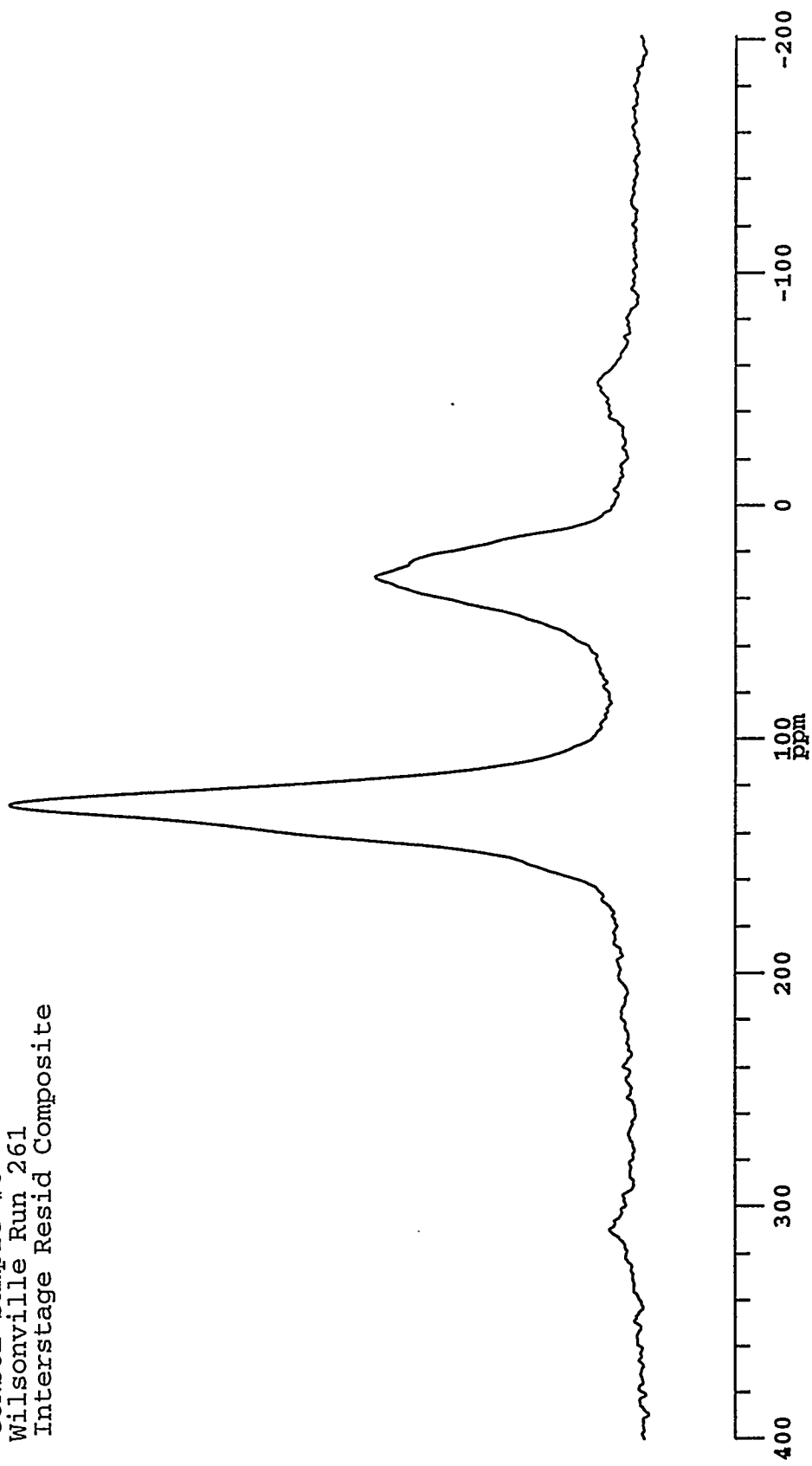
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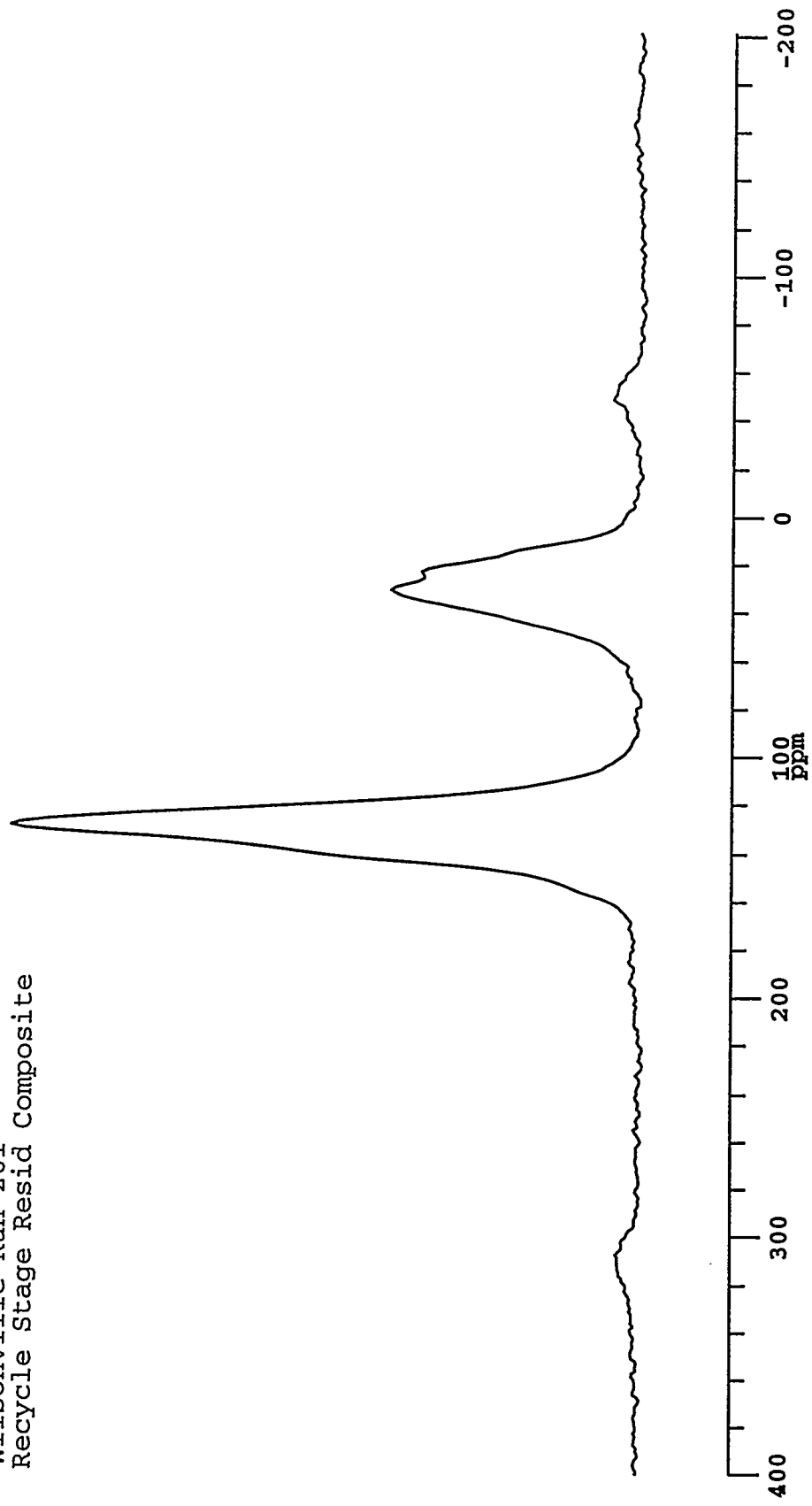
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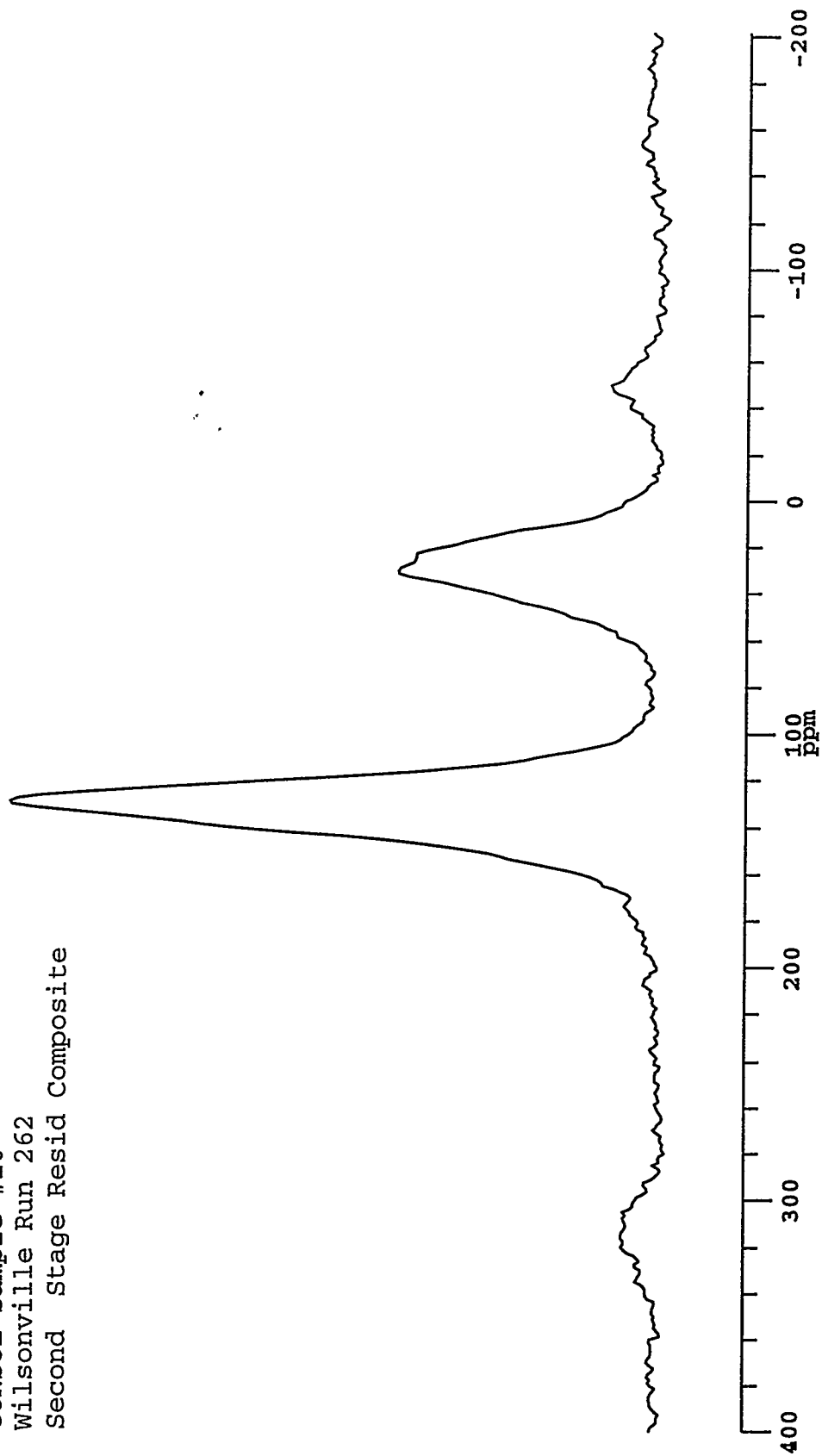
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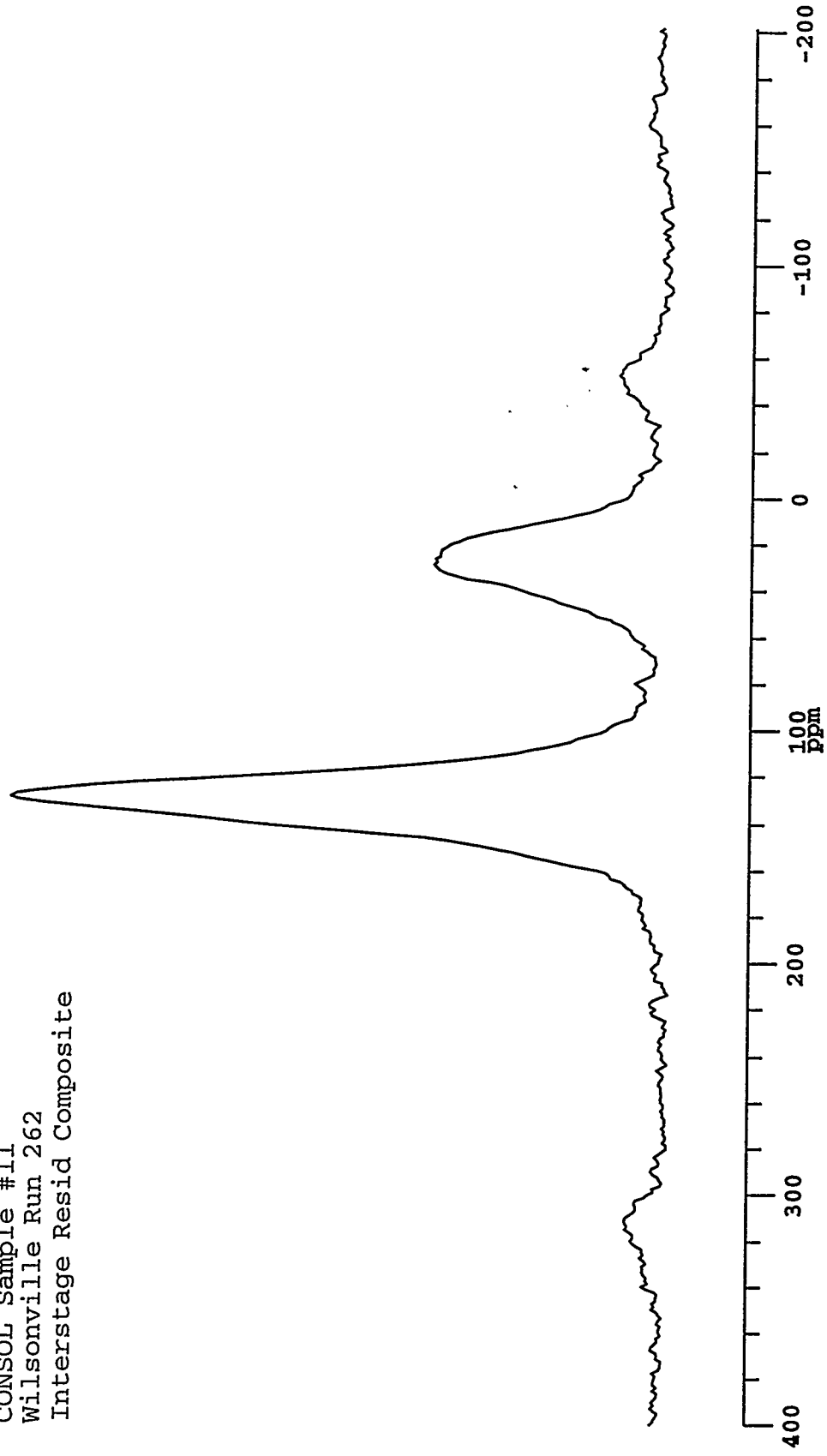
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CONSOL Sample #13
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Recycle Stage Resid Composite

CONSOL Sample #14
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O-43

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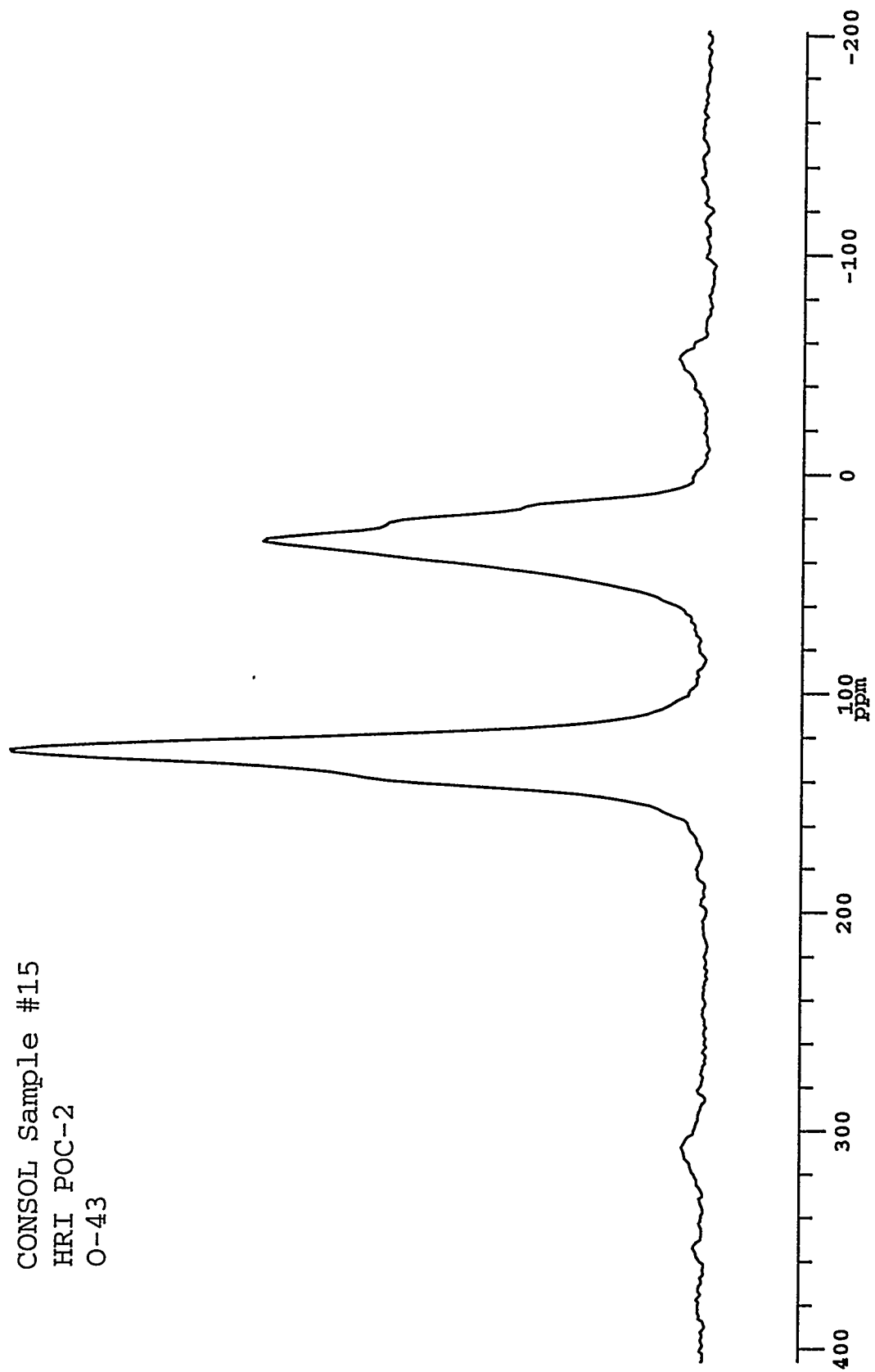
APPENDIX 6

UNIVERSITY OF DELAWARE QUARTERLY REPORT

THE KINETICS OF COAL LIQUEFACTION DISTILLATION RESID CONVERSION

QUARTERLY REPORT
7/15/95-10/15/95

Michael T. Klein
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Date Published
October 27, 1995

QUARTERLY REPORT

RESID CONVERSION KINETICS

A number of hydrocracking reactor runs have been made with Wilsonville Run 258 resid under a variety of conditions and with two catalysts (sulfided molybdenum naphthenate and Ni-Mo on alumina) A list of these runs is given in Table 1.

As pointed out in the last monthly report, we have determined the conversion of Wilsonville Run 258 resid to material boiling below 850°F to be about 30 % in one hour and about 18 % in 30 minutes. This is using 1500 psi hydrogen, 0.9 % sulfided molybdenum naphthenate. 3/1 tetralin to resid ratio and 312 °C. The conversion runs made to date are shown in Table 2. Since the conversion is determined as the product of the amount of resid solubilized and the percentage of product boiling below 850°F, the errors in either or both measurements result in compounding of errors. To remove some of the uncertainty and establish the reproducability in these figures. ten runs have been made at 435°C and 30 minutes, five with 0.9 % sulfided molybdenum naphthenate catalyst and five with no catalyst. These runs are listed in Table 3. The conversion calculation is based on Equation 1:

$$Conversion\ (850\ °F^-) = TSF \times (\ 1\ -\ \frac{850\ °F^+\ in\ tetralin}{RSF\ in\ Tetralin}\ ) \tag{1}$$

Where the Tetralin Soluble Fraction (TSF) is determined by ash content in the solid residue after resid processing; Resid Soluble Fraction (RSF) and 850 °F$^+$ fractions in tetralin are determined by running the ramp and SimDis TG methods on the liquid products, respectively.

The analytical work to determine the conversions by this method is very time consuming and is not yet finished. It will be included in the next report.

We have also made several resid hydrocracking runs in the presence of coal. since coal is presence in the resid recycled to the reactor. These are runs listed in Table 4. Again, the actual conversions are not yet determined although the runs ran smoothly in the presence of both coal and resid.

As soon as time permits, we plan to make hydrocracking runs with the same resid using a range of concentrations of sulfided molybdenum naphthenate, to determine the rate of resid break-down at a molybdenum concentration in a more economic range.

MODELING

Construction of a molecular representation for a resid has recently been updated. A molecule is considered to be a collection of attributes (e.g. number of aromatic rings, number of naphthenic rings, etc.) and the attribute values are associated with a probability

1

density function (pdf). By stochastically sampling these pdf's a representation of approximately 10,000 molecules can be constructed which accurately represents a selected resin. Recent investigations have shown that the information within these pdf's can also be represented with a smaller number of molecules (10-100).

Construction of a small set of molecules allows construction of a deterministic reaction model by solving a set of material balance ordinary differential equations (ODE's). The traditionally Monte Carlo reaction approach requires determining each time step and reaction event one at a time which is CPU intensive. Solving a set of ODE's using software from the public domain requires only a small amount of computing time (ca. 1 second).

Most of the necessary analytical information for the CONSOL resids has been provided. Elemental analyses, resid molecular weights using FIMS, and proton NMR data have been provided. All SARA (saturates, aromatics, resins, asphaltenes, and pre-asphaltenes) fractions for the CONSOL resids have been received. To date, molecular weights have been determined for each of the aromatic fractions and a couple of the resin fractions. Dichlorobenzene is used for the aromatics, resins and the asphaltene fractions. Toluene is used for the saturate fractions and initially THF or pyridine is used for the pre-asphaltene fractions. Listed in the table 5 below are the results to date.

ANALYTICAL DEVELOPMENT

The Netzsch Thermogravimetric Analyzer for coupling to the mass spectrometer in the Chemistry Department for running coal liquids and resids mentioned in the previous quarterly report was tested. It was found to be very sensitive to vibration and also to have problems with the temperature control system. As a result, the instrument was returned for repairs and a mounting to eliminate most of the vibration was constructed. The instrument problems now appear to have been corrected however there is still a problem with the software which should not be too difficult to correct. Netzsch tells us they are working to correct the software.

QUART RLY REPORT

RESID CONVERSION KINETICS

A number of hydrocracking reactor runs have been made with Wilsonville Run 258 resid under a variety of conditions and with two catalysts (sulfided molybdenum naphthenate and Ni-Mo on alumina) A list of these runs is given in Table 1.

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As soon as time permits, we plan to make hydrocracking runs with the same resid using a range of concentrations of sulfided molybdenum naphthenate, to determine the rate of resid break-down at a molybdenum concentration in a more economic range.

MODELING

Construction of a molecular representation for a resid has recently been updated. A molecule is considered to be a collection of attributes (e.g. number of aromatic rings, number of naphthenic rings, etc.) and the attribute values are associated with a probability

1

Table 1 List of reactor runs (P=1500 psig)

Run	T, C	t, min	Catalyst	SA	T:R	Gas	Rec., wt%
C001	19	15			3	H2	79.8%
C002	414	15			3	N2	25.5%
C003	408	15			3	H2	73.6%
C004	410	7			3	N2	74.3%
C005	409	15			3	N2	84.4%
C006	411	15		Yes	3	H2	91.2%
C007	408	15		Yes	3	N2	76.5%
C008	406	15	Mo-naph	Yes	3	N2	98.1%
C009	408	15	Mo-naph	Yes	3	H2	76.3%
C012	400	15	Mo-naph		3	N2	42.6%
C013	400	15	Mo-naph		3	N2	38.0%
C014	392	15	Mo-naph		5	N2	55.2%
C015	403	15	Mo-naph		3	H2	92.6%
C016	406	15	Mo-naph		3	N2	38.7%
C017	409	0.06	Mo-naph	Yes	3	H2	80.2%
C018	408	1	Mo-naph	Yes	3	H2	76.3%
C019	412	3	Mo-naph	Yes	3	H2	62.1%
C020	410	5	Mo-naph	Yes	3	H2	91.3%
C021	411	10	Mo-naph	Yes	3	H2	95.1%
C022	408	30	Mo-naph	Yes	3	H2	80.9%
C023	422	40	Mo-naph	Yes	3	H2	68.5%
C024	408	60	Mo-naph	Yes	3	H2	95.4%
C025	419	0.06	Mo-Ni/Alumina		2	H2	47.5%
C026	420	1	Mo-Ni/Alumina		2	H2	54.4%
C027	410	3	Mo-Ni/Alumina		2	H2	66.2%
C028	409	5	Mo-Ni/Alumina		2	H2	65.2%
C029	410	10	Mo-Ni/Alumina		4	H2	69.4%
C030	400	15	Mo-Ni/Alumina		2	H2	36.2%
C031	405	15	Mo-Ni/Alumina		3	H2	49.1%
C032	405	15	Mo-Ni/Alumina		4	H2	80.5%
C033	412	60	Mo-Ni/Alumina		4	H2	70.6%
C034	405	30	Mo-Ni/Alumina		4	H2	72.8%
C035	21	0			3	Tetralin washing	
C036	21	0			3	THF washing	
C037	21	0	Mo-Ni/Alumina		3	Tetralin washing	
C038	27	15			3	N2	69.8%
C039	27	15	Mo-Ni/Alumina		3	N2	53.3%
C040	27	15	Mo-naph	Yes	3	N2	71.5%
C041	432	30	Mo-naph	Yes	3	H2	76.2%
C042	436	60	Mo-naph	Yes	3	H2	93.3%

Table 2 Preliminary Results of the Resid Conversion

Name	T C	t min	Catalyst	SA g	Gas	Ash (TGA) wt%	TSF wt%	RSF in Tetralin wt%	850 F+ in Tetralin wt%	Conversion wt%
Reisd					–	16.2%	–			
C001	19	15			H2	35.7%	54.7%	3.74%	3.56%	2.6%
C006	411	15		1	H2	43.3%	62.6%	9.82%	7.68%	13.6%
C007	408	15		1	N2	40.7%	60.2%	11.81%	8.69%	15.9%
C008	406	15	Mo-naph.	1	N2	37.4%	56.7%	10.46%	8.28%	11.8%
C009	408	15	Mo-naph.	1	H2	45.4%	64.4%	10.95%	6.73%	24.8%
C014	392	15	Mo-naph.		N2	42.6%	62.0%	9.69%	8.92%	4.9%
C015	403	15	Mo-naph.		H2	46.0%	64.8%	9.51%	6.83%	18.3%
C017	409	0.06	Mo·naph.	1	I!2	40.3%	59.9%	7.02%	5.42%	13.6%
C018	408	1	Mo-naph.	1	H2	42.7%	62.1%	10.91%	7.94%	16.9%
C019	412	3	Mo-naph.	1	H2	41.4%	60.9%	13.74%	10.79%	13.1%
C020	410	5	Mo-naph.	1	H2	44.2%	63.4%	9.34%	7.35%	13.5%
C021	411	10	Mo-naph.	1	H2	42.0%	61.4%	11.18%	7.78%	18.7%
C022	408	30	Mo-naph.	1	H2	46.0%	64.9%	14.33%	10.23%	18.6%
C024	408	60	Mo-naph.	1	H2	51.8%	68.8%	12.96%	7.28%	30.1%

Table 3 List of multiple reactor runs (P=1500 psig)

Run	T, C	t, min	Catalyst	SA	T:R	Gas	Rec., wt%
C047	435	30	Mo-naph	Yes	3	H2	89.6%
C048	435	30	Mo-naph	Yes	3	H2	92.9%
C049	436	30	Mo-naph	Yes	3	H2	89.7%
C050	436	30	Mo-naph	Yes	3	H2	91.5%
C051	437	30	Mo-naph	Yes	3	H2	78.7%
C052	437	30			3	H2	89.7%
C053	436	30			3	H2	80.5%
C054	436	30			3	H2	88.0%
C055	437	30			3	H2	72.1%
C056	436	30			3	H2	83.3%

Table 4 List of co-processing reactor runs (P=1500 psig)

Run	T, C	t, min	Catalyst	SA	Resid:Coal*	T:R or T:C or T:(R+C)	Gas	Rec., wt%
C043	420	30	Mo–naph	Yes	Coal only	3	H2	43.1%
C044	420	60	Mo–naph	Yes	Coal only	3	H2	61.4%
C045	436	30	Mo–naph	Yes	2	3	H2	96.1%
C046	435	60	Mo–naph	Yes	2	3	H2	82.7%

Black Thunder coal

Table 5   Analytical Results of the Resids

Sample #	Saturate MW	Aromatic MW	Resin MW	Asphaltene MW	Pre-Asphaltene MW
1		320			
2		274	613		
3		319	568		
4		362			
5		493			
6		420			
7		348			
8		425			
9		323			
10		430			
11		386			
12		413			
13		336			
14		356			
15		345			